Intermediates in the Palladium-Catalysed Reactions of 1,3-Dienes, Part 5 [1] Butadiene Complexes of Nickel, Palladium and Platinum

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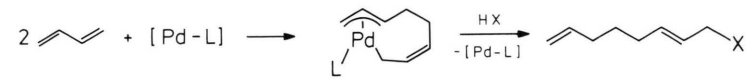
Nickel-organo Complex, Palladium-organo Complex, Platinum-organo Complex, Butadiene Complex

A series of $[M(R_2PC_2H_4PR_2)(butadiene)]$ complexes of Ni, Pd and Pt has been prepared and their structures investigated NMR-spectroscopically. The nickel and palladium complexes, irrespective of the substituents at phosphorus, contain a fluxional η^2-bonded butadiene molecule. In the case of platinum the bonding mode is ligand dependent: an η^2-arrangement is observed where R is *tert*-butyl or cyclohexyl while when R is isopropyl the butadiene adopts an η^1,η^1-arrangement to give a platinacyclopentene derivative.

Introduction

The course of the palladium-catalysed telomerization of 1,3-dienes with nucleophiles is dependent upon the coordinating properties of the donor ligand associated with the metal [3]. In the presence of monodentate ligands, 2:1 telomers (octadiene derivatives) are formed whereas the introduction of a bidentate chelating ligand directs the reaction towards 1:1 telomers (butene derivatives). In a previous publication in this series [4], we presented evidence suggesting that octadienediyl-palladium species are involved as intermediates in the formation of the octadiene derivatives (eq. (1)). In an attempt to gain further insight into the mechanism of the formation of the butene derivatives, we have prepared a series of $[M(R_2PC_2H_4PR_2)(butadiene)]$ derivatives of nickel, palladium and platinum and have investigated their reactions with nucleophiles. The preparation and structure of these complexes is discussed here while their reactions are discussed in a following paper.



(1)

Preparation of the Complexes

At the beginning of this investigation information on the $[ML_2(butadiene)]$ complexes was essentially limited to a brief mention of $[Ni(Cy_2PC_2H_4PCy_2)(C_4H_6)]$ [5] and the platinum complex $[Pt(PPh_3)_2(C_4H_6)]$ [6]. Subsequently, a number of complexes of this type involving substituted 1,3-dienes have been reported: nickel complexes containing isoprene [7], allylidenecyclopropane [8] and dimethylpenta-2,4-dienoate [9], palladium complexes with allylidenecyclopropane [8] and platinum complexes involving 2,3-dimethyl- and 2,3-diphenylbutadiene [10].

The palladium complexes (**1–4**) discussed here were prepared by reacting bis(η^3-allyl)palladium with the chelating phosphine and butadiene (eq. (2)). The nickel (**5**) and platinum (**6–8**) complexes were prepared by reacting the appropriate bis(1,5-cyclooctadiene)metal species with the chelating ligand in a mixture of ether and butadiene (eq. (3)).

$$[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)_2] + R_2PC_2H_4PR_2 + C_4H_6 \xrightarrow{-C_8H_{14}} [Pd(R_2PC_2H_4R_2)(C_4H_6)] \quad (2)$$

1: R = Pr^i; **2:** R = Bu^t; **3:** R = Cy; **4:** R = Ph

$$[M(cod)_2] + R_2PC_2H_4PR_2 + C_4H_6 \xrightarrow{-2\ cod} [M(R_2PC_2H_4PR_2)(C_4H_6)] \quad (3)$$

5: M = Ni, R = Cy; **6:** M = Pt, R = Pr^i;
7: M = Pt, R = Bu^t; **8:** M = Pt, R = Cy

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3 could also be prepared in over 80% yield by reducing palladium acetate with magnesium-anthracene in the presence of the diphosphine and butadiene (eq. (4)).

$$1/3[Pd(OAc)_2]_3 + Mg(anth) + Cy_2PC_2H_4PCy_2 + C_4H_6 \rightarrow \mathbf{3} + anth + Mg(OAc)_2 \quad (4)$$

The butadiene complexes are relatively stable in the solid state at 0 °C but should be stored at low temperature. The nickel complexes are orange-yellow, the palladium complexes pale yellow and the platinum complexes white. In most cases a parent ion was observed in the mass spectra. In some cases, *e.g.* **3** and **4,** the presence of butadiene was also confirmed by displacement reactions with CO or hydrogenation. Reaction of **3** with allene, CS_2 or dimethylacetylenedicarboxylate also resulted in displacement of the diene to give L_2Pd-η^2-allene, $-CS_2$, or -alkyne complexes [1].

Structure of the η^2-Butadiene Complexes

The structural investigation of the $[M(R_2PC_2H_4PR_2)(C_4H_6)]$ complexes (M = Ni, Pd, Pt) was carried out using standard spectroscopic methods and was supported by a partial crystal structure determination of $[Pd(Bu^t_2PC_2H_4PBu^t_2)(\eta^2\text{-}C_4H_6)]$. A number of factors, including lack of solubility and viscosity of the samples at low temperature, prevented us from obtaining satisfactory solution spectra for all of the complexes and the discussion is limited to those systems for which unequivocal information was obtained. The complete spectroscopic data have been collected together in Tables I and II.

$[Pd(R_2PC_2H_4PR_2)(\eta^2\text{-}C_4H_6)]$ complexes

The infrared spectrum of **1** (R = Pr^i) has an absorption at 1601 cm^{-1} which is attributed to an uncomplexed double bond. The ^{31}P NMR spectrum of this complex is that of an AB spin system (−80 °C, δ_A 63.4, δ_B 55.2, J_{AB} 50.6 Hz) and remains sharp from 0 down to −80 °C indicating that the two phosphorus atoms are inequivalent over the whole of this temperature range. On the other hand, the ^1H and ^{13}C NMR spectra indicate fluxionality: only 3 signals (instead of the 6 expected for an η^2-complex) are observed for the butadiene protons over the temperature range 0 to −100 °C. The ^{13}C NMR spectrum at −10 °C contains only two signals, both broad, attributable to the diene; the signal at 70.2 ppm is assigned to the terminal C-atoms (C1, C4) on the basis of its multiplicity in the proton-coupled spectrum (t, J_{CH} 154 ± 2 Hz), and the signal at 103.8 ppm is assigned to the internal C-atoms (C2, C3; d, J_{CH} 150 ± 2 Hz). The exchange is slowed down sufficiently at −115 °C for 4 broad signals to be observed. The chemical shifts of these signals indicate that equilibration involves exchange of C1 (39.1 ppm) with C4, (100.0 ppm) (av. shift 69.6 ppm) and of C2 (60.1 ppm) with C3 (146.4 ppm), (av. shift 103.3 ppm). The broadness of the absorptions at both −115 °C and −10 °C indicates that at the lower temperature exchange is not completely frozen out and at higher temperatures it is still relatively slow. Similar effects were observed in the NMR spectra of **2** (R = Bu^t) and **3** (R = Cy).

An X-ray diffraction study of **2** [11] confirms that, in the crystal, the butadiene molecule occupies a single-*trans*, η^2-configuration (Fig. 1).

Although disorder prevented refinement of the data below an *R*-factor of 0.0566 (R_w = 0.076), the geometry of the molecule is clearly established: the P-atoms, the metal atom and C1 lie in the same plane while the butadiene adopts a single-*trans* geometry and is complexed as an η^2-ligand. The disorder arises since the butadiene moiety adopts two conformations in the crystal with the uncomplexed double bond being either above or below the plane. In both configurations, the non-complexed double bond has the same phosphorus atom as its next neighbour.

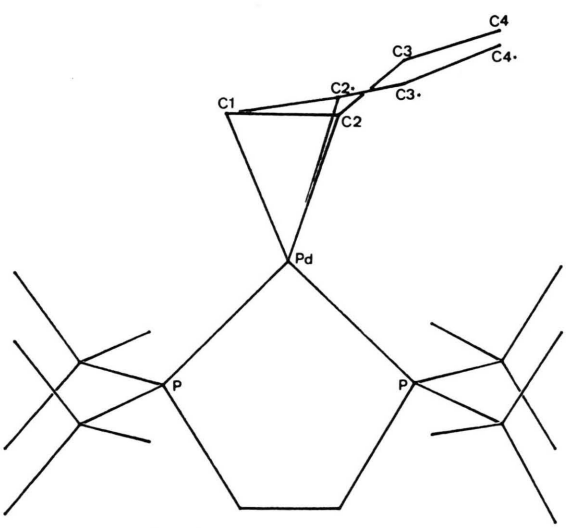


Fig. 1. The molecular structure of $[Pd(Bu^t_2PC_2H_4PBu^t_2)(\eta^2\text{-}C_4H_6)]$ (**2**).

[Pt(R$_2$PC$_2$H$_4$PR$_2$)(η^2-C$_4$H$_6$)] complexes

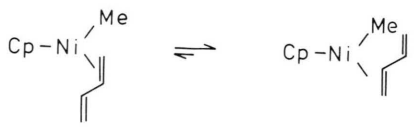
The structures of the platinum complexes **7** (R = Bu^t) and **8** (R = Cy) are analogous to the palladium systems discussed above. The infrared spectrum of **7** has an absorption at 1600 cm^{-1} attributable to the free double bond. The ^{31}P NMR spectrum (Fig. 2) is that of an ABX spin system (A, B = ^{31}P, X = ^{195}Pt) with nearly identical coupling to platinum.

The M–C bond in the platinum-butadiene complexes may be expected to be stronger than that in the corresponding complexes of nickel and palladium and as a result exchange processes should be slower. In agreement with this, the ^{13}C NMR spectrum of **7** (R = Bu^t) at −45 °C has 4 sharp multiplets assignable to the butadiene C-atoms (Fig. 3).

The carbon atoms C1 and C2 couple to both phosphorus atoms whereby the observation of a large and a small coupling ($^2J_{C,P}$) is consistent with a *quasi*-square planar arrangement about the metal atom; the magnitude of the *trans* coupling being greater than that of the *cis*. C3 couples with both P-atoms, C4 with only one.

The ^{1}H NMR spectrum of **7** at −80 °C is also that of a static system and 6 signals for the 6 different butadiene protons are observed (Fig. 4).

Particularly significant is the value for $J_{1,4}$ of 10.4 Hz; this is practically identical to that observed in free butadiene [12], which adopts mainly a single-*trans* configuration, and is very similar to that found in **9a** (10.5 Hz) and **9b** (9.8 Hz) for which a single-*trans* arrangement has been assumed [13].



(a) **9** (b)

Moreover an exchange between H1 and H4, *i.e.* between the uncomplexed and complexed double bonds, has been demonstrated by a magnetization transfer experiment. In addition to the ^{31}P, ^{1}H and ^{13}C NMR spectra, the ^{195}Pt spectrum of **7** has been recorded in the hope of gaining information on the oxidation state of the metal. This and related results have been discussed in a previous publication [14] and it is sufficient to mention here that the data (δ^{195}Pt = 5230 ppm, $J_{P1,Pt}$ 3248 Hz, $J_{P2,Pt}$ 3227 Hz) fall in the range observed for zerovalent-platinum complexes.

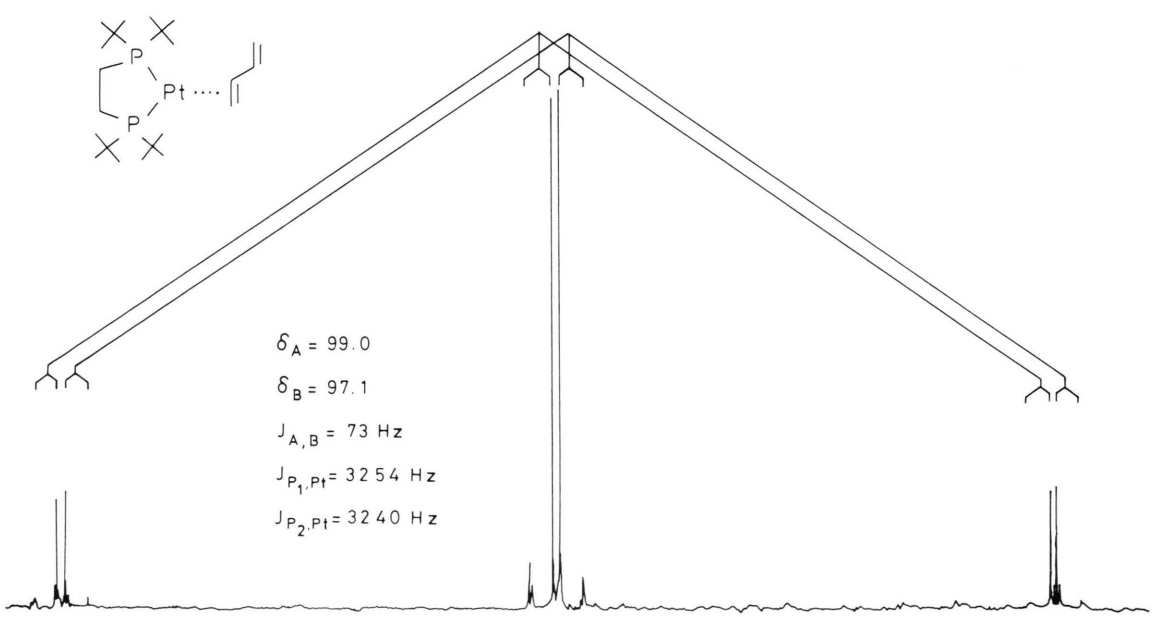


Fig. 2. ^{31}P NMR spectrum of [Pt(Bu$^t_2$PC$_2$H$_4$PBu$^t_2$)(η^2-C$_4$H$_6$)] (**7**) (32.4 MHz, −30 °C, d$_8$-THF).

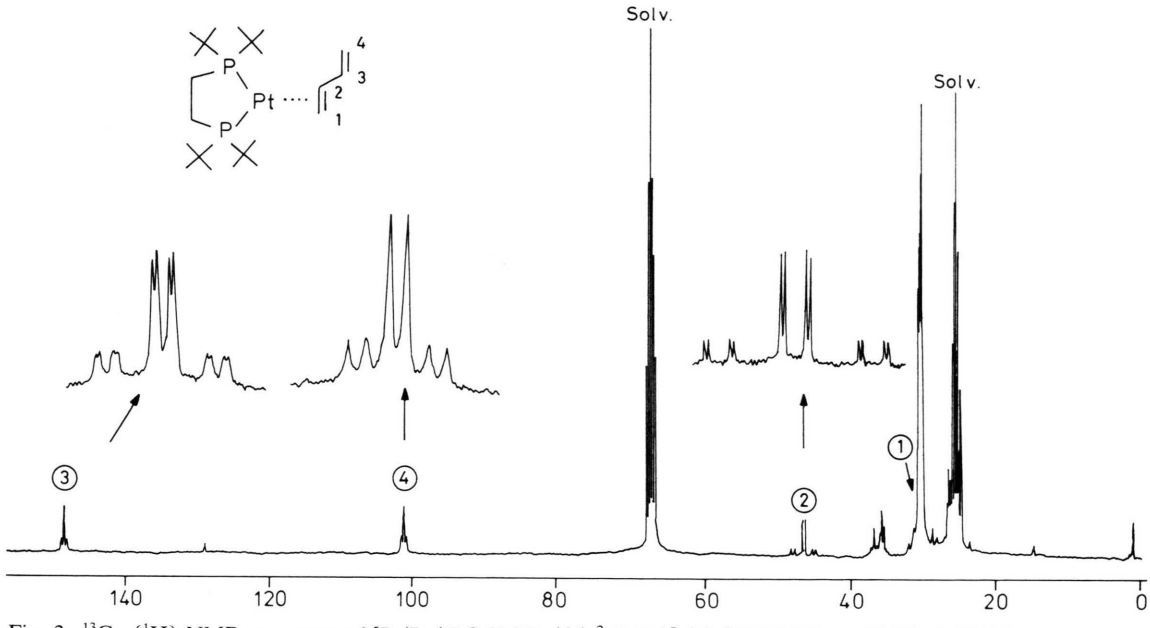
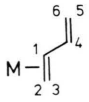


Fig. 3. $^{13}C-\{^1H\}$ NMR spectrum of $[Pt(Bu^t_2PC_2H_4PBu^t_2)(\eta^2\text{-}C_4H_6)]$ (**7**) (75.5 MHz, −45 °C, d_8-THF).

Table I. ^1H NMR data for the $[M(R_2PC_2H_4PR_2)(\eta^2\text{-}C_4H_6)]$ complexes (M = Pd, Pt; R = Pr^i, Bu^t, Cy).

Complex (M, R)	δ(*J*) δBD[a]	J_{BD} [Hz]	δLig[b]	J_{Lig} [Hz]
1 (Pd, Pr^i) (400 MHz, −80 °C, d_8-THF)	4.88 (m, H1/4) 3.28 (m, H2/3, 5/6)	–	2.01 (m, H7/10), 1.08 (dd, H8) 1.07 (dd, H9), 1.01 (dd, H11) 0.99 (dd, H12), 1.66 (m, H13)	$J_{7,8}$ 6.9 $J_{7,P}$ 6.8, $J_{8,P}$ ~14.0 $J_{13,P}$ 32.0
2 (Pd, Bu^t) (400 MHz, −30 °C, d_8-THF)	4.87 (m, H1/4) 3.44 (m, H2/3, 5/6)	–	1.19 (d, H8), 1.17 (d, H10)	$J_{8,P} \sim J_{10,P}$ 17.5
3 (Pd, Cy) (80 MHz, −30 °C, d_8-tol)	5.55 (m, H1/4) 3.92 (m, H2/5) 4.12 (m, H3/6)	$J_{1,2}$ 8.5, $J_{1,3}$ 13.5 $J_{2,P}$ 3.5, $J_{3,P}$ 3.5	br	–
7 (Pt, Bu^t) (400 MHz, −80 °C, d_8-THF)	1,96 (m, H2) 2.98 (m, H1) 1.74 (m, H3) 5.53 (m, H4) 4.09 (m, H5) 4.53 (m, H6)	$J_{1,2}$ 8.6, $J_{1,3}$ 9.8 $J_{1,4}$ 10.4, $J_{2,3}$ 4.7 $J_{4,5}$ 9.8, $J_{4,6}$ 16.8 $J_{5,6}$ 2.5, $J_{4,P}$ 2.3 $J_{5,P}$ 4.6, $J_{6,P}$ 4.5 $J_{2,Pt}$ 51.6, $J_{1,Pt}$ 63.0 $J_{5,Pt}$ 24.4, $J_{6,Pt}$ 20.8	1.22 (d, H7), 1.21 (d, H8) 1.20 (d, H9), 1.14 (d, H10) 1.96 (m, H11), 1.57 (m, H12)	$J_{7,P}$ 12.3, $J_{8,P}$ 12.2 $J_{9,P}$ 12.2, $J_{10,P}$ 12.1
8 (Pt, Cy) (400 MHz, −80 °C, d_8-THF)	3.05 (m, H1) 5.51 (m, H4) 4.03 (m, H5) 4.56 (m, H6)	$J_{1,2} \sim J_{1,3}$ 9.1, $J_{4,5}$ 10.0 $J_{4,6}$ 16.7, $J_{4,1}$ 10.2 $J_{5,6}$ 2.5, $J_{1,P1}$ 4.3 $J_{1,P2}$ 9.4, $J_{4,P}$ 2.2 $J_{5,P}$ 4.7, $J_{6,P}$ 4.4 $J_{1,Pt}$ 61	br	–

a



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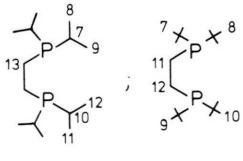


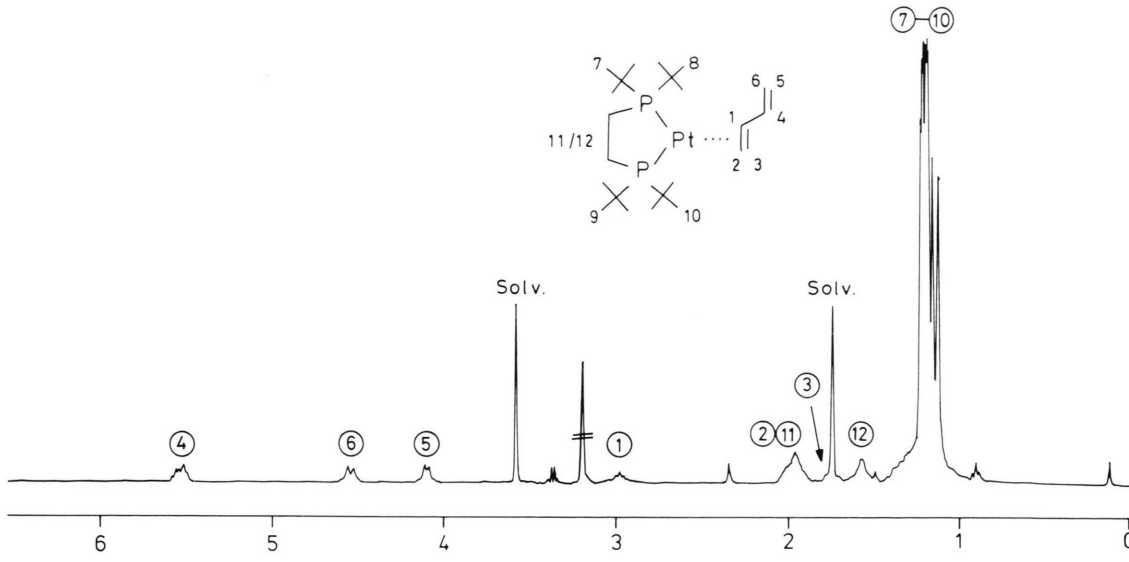
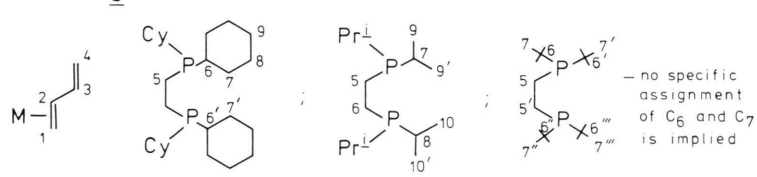


Fig. 4. ^1H NMR spectrum of $[Pt(Bu^t_2PC_2H_4PBu^t_2)(\eta^2\text{-}C_4H_6)]$ (**7**) (400 MHz, −80 °C, d_8-THF).

Table II. $^{13}C-\{^1H\}$ NMR data for the $[M(R_2PC_2H_4PR_2)(\eta^2\text{-}C_4H_6)]$ complexes (M = Pd, Pt; R = Pr^i, Bu^t, Cy).

Complex (M, R)	$\delta Cn(J)$ δC_{BD}[a]	J_{BD} [Hz]	δC_{Lig}[b]	J_{Lig} [Hz]
1 (Pd, Pr^i) (75.5 MHz, −115 °C, d_8-THF)	39.1 (C1) 60.1 (C2) 146.4 (C3) 100.0 (C4)	–	22.15 } C 5/6 21.30 }	$J_{C5,P1}$ ($J_{C5,P2}$) 18.3 $J_{C6,P1}$ ($J_{C6,P2}$) 17.8
1 (Pd, Pr^i) (75.5 MHz, −10 °C, d_8-THF)	70.1 (C1/4) 103.6 (C2/3)	$J_{C1/4,H}$ 154±2 $J_{C2/3,H}$ 150±2	22.97, 22.26 (C5/6) 25.95, 25.65 (C7/8) 20.34, 19.80 (C9/9′, 19.31, 18.97 (C10/10′)	$J_{C5/6,P1}$ 16.5 $J_{C5/6,P2}$ 19.4, 18.8 $J_{C7,P1/2}$ 4.1, 8.4 $J_{C8,P1/2}$ 3.9, 9.1
3 (Pd, Cy) (25.5 MHz, −102 °C, d_8-THF)	40 (C1) 60 (C2) 148 (C3) 101 (C4) } br			
3 (Pd, Cy) (25.5 MHz, 20 °C, d_8-THF)	70.2 (C1/4) 103.8 (C2/3)			
7 (Pt, Bu^t) (75.5 MHz, −45 °C, d_8-THF)	29.9 (C1) 46.4 (C2) 148.6 (C3) 101.1 (C4)	$J_{C1,P1}$ 39.7, $J_{C2,P2}$ 6.1 $J_{C2,P1}$ 35.6, $J_{C2,P2}$ 5.6 $J_{C3,P1}$ 7.9, $J_{C3,P2}$ 2.3 $J_{C4,P}$ 8.1, $J_{C1,Pt}$ 242.9 $J_{C2,Pt}$ 219.3, $J_{C3,Pt}$ 52.7 $J_{C4,Pt}$ 39.2	25.0−26.7 (C5/5′) 36.8 (C6), 35.9 (C6′) 35.7 (C6″), 35.4 (C6‴) 30.51 (C7), 30.34 (C7′) 30.13 (C7″), 30.05 (C7‴)	$J_{C6,P1}$ 13.2, $J_{C6,P2}$ 5.1 $J_{C6',P1}$ 13.5, $J_{C6',P2}$ 3.9 $J_{C6'',P1}$ 12.7, $J_{C6'',P2}$ 3.6. $J_{C6''',P1}$ 14.2, $J_{C6''',P2}$ 5.6 $J_{C7,P}$ 6.1, $J_{C7',P}$ 6.6 $J_{C7'',P}$ 5.6, $J_{C7''',P}$ 6.1 $J_{C6,Pt}$ 51.7, $J_{C6',Pt}$ 50.9 $J_{C6'',Pt}$ 47.8, $J_{C6''',Pt}$ 55.5
8 (Pt, Cy) (75.5 MHz, −100 °C, d_8-THF)	n.d. (C1) 45.4 (C2) 148.5 (C3) 100.1 (C4)	$J_{C2,P}$ 34	–	–

a b



Exchange mechanism

Any single mechanism which accounts for the dynamic behaviour of the $[M(R_2PC_2H_4PR_2)(\eta^2\text{-}C_4H_6)]$ complexes of Pd and Pt discussed above must accomodate the following observations: the butadiene molecule is η^2-bonded to the metal-atom, the two phosphorus atoms remain magnetically inequivalent over the whole of the temperature range of the exchange process, the metal-bonded carbon and phosphorus atoms adopt a square planar arrangement, the η^2-butadiene molecule has a single-*trans* configuration and the two double bonds of the butadiene molecule are involved in the exchange process.

A mechanism consistent with these observations is shown as Scheme 1.

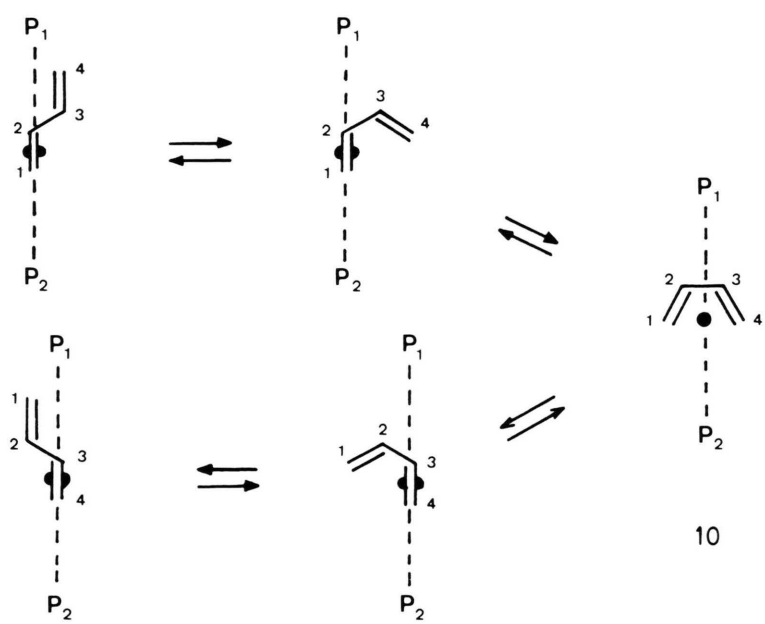
The η^2-bonded, single-*trans* butadiene molecule adopts a single-*cis* configuration as the result of rotation about the C2–C3 axis. This is followed by conversion into an intermediate **10** having a pseudo-tetrahedral geometry with an η^4-bonded butadiene. **10** can rearrange further either to give the original situation or with exchange of the double-bond coordinated to the metal.

The spectra rule out a number of alternative mechanisms. For example, the intermediate formation of a metallacyclopentene ring would lead to equilibration of the P-atoms while a simple rotation of the butadiene molecule about the metal axis would also lead to equilibration but would not cause exchange of the two double bonds. The conservation of the P–P and Pt–P couplings indicates, moreover, that the exchange is not *inter*molecular.

$[Ni(Cy_2PC_2H_4PCy_2)(\eta^2\text{-}C_4H_6)$

The results described above enable us to interpret those obtained for the nickel-butadiene complex (**5**). A band at 1590 cm^{-1} in the infrared spectrum indicates the presence of a free double bond. The ^{31}P NMR spectrum at −30 °C is that of an AB spin system with a relatively small coupling J_{AB} (Fig. 5). Upon reducing the temperature further, the low field doublet broadens and moves to lower field, eventually becoming a single broad line at −90 °C while the high field doublet remains relatively sharp and moves only slightly to higher field (δ_A = 78.0 at −30 °C and 90 at −110 °C; δ_B = 51.4 and 49.6 at the same temperatures). This effect appears to be the result of a temperature dependent equilibrium between two rapidly exchanging species having similar ^{31}P NMR spectral parameters: the high field signals of the spectra of these species have nearly the same chemical shifts. Above −30 °C exchange of A and B takes place and at room temperature a broad singlet is observed.

The ^{13}C NMR spectrum of **5** also differs from those of the corresponding Pd and Pt complexes. At



Scheme 1.

40 °C the butadiene signals at 61.5 (CH_2) and 95.0 ppm (CH) are relatively sharp. On cooling the sample they become broader and both are shifted considerably to higher field (*i.e.*, at −110 °C to *ca.* 47 and 85 ppm, respectively). No splitting of the signals was observed. These results also indicate that a temperature dependent equilibrium with rapid exchange is present. The observed variations of the chemical shifts suggest that at higher temperature the compound containing η^2-bound butadiene is preferred but that an increasing population of a complex with η^4-bound butadiene is formed at lower temperature. The structure of the latter compound is probably similar to that of the intermediate **10** postulated for Pd and Pt. This explanation is also consistent with the ^{31}P NMR and IR spectroscopic evidence given above.

Miscellaneous results

A number of anomalous observations complicate the interpretation discussed above. The bis(diphenylphosphino)ethane stabilized palladium complex **4** has the expected absorption at 1600 cm^{-1} in the infrared spectrum and reaction with CO leads to the quantitative displacement of butadiene, however, the ^{31}P NMR spectrum from R.T. to −110 °C consists of a sharp singlet instead of the expected doublet of doublets while in the ^1H and ^{13}C NMR spectra the butadiene molecule could not be detected. Presumably additional dynamic effects are responsible and these could include free rotation about the metal-butadiene axis, exchange with free butadiene and dissociation of one phosphorus atom from the metal. Similar observations have been reported for $[Pt(PPh_3)_2(\eta^2\text{-}C_4H_6)]$ [6].

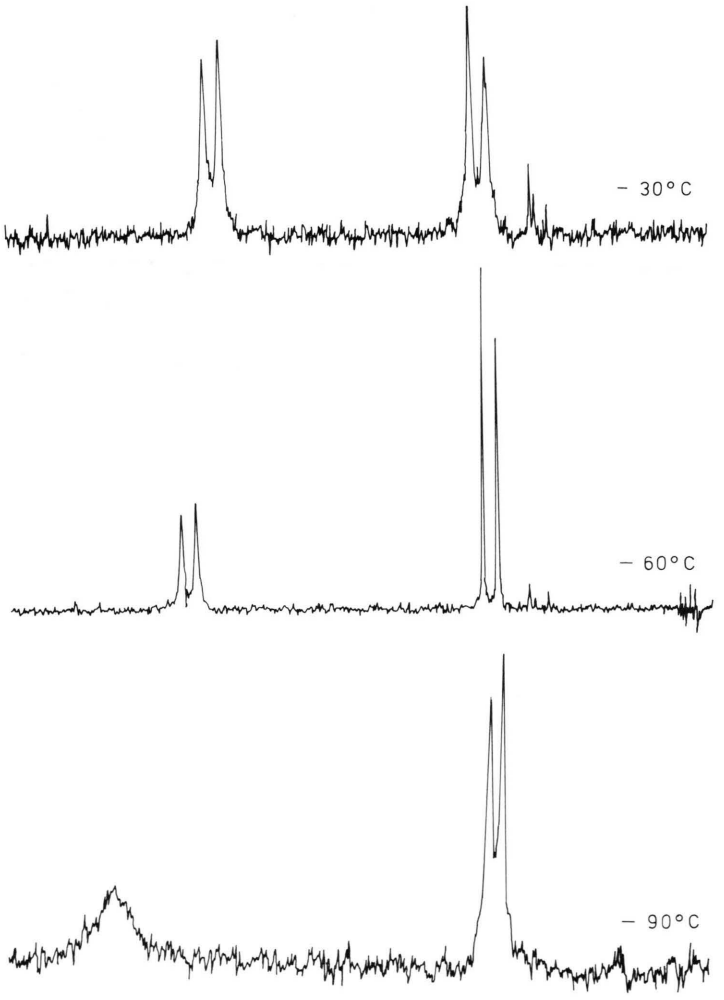


Fig. 5. ^{31}P NMR spectra of $[Ni(Cy_2PC_2H_4PCy_2)(\eta^2\text{-}C_4H_6)]$ (**5**) (32.4 MHz, d_8-toluene).

We have also prepared related complexes of 1,3-cyclohexadiene in the hope that these would serve as models for systems containing single-*cis* butadiene. $[Pd(Cy_2PC_2H_4PCy_2)(\eta^2\text{-}1,3\text{-}C_6H_8)]$. C_6H_8 (**11**) was prepared from bis(η^3-allyl)palladium and $[Pt(Cy_2PC_2H_4PCy_2)(\eta^2\text{-}1,3\text{-}C_6H_8)]$ (**12**) was the product of diene exchange with the platinum-butadiene complex (**8**). Neither of these reactions could be extended to nickel. The ^{31}P NMR spectra of **11** and **12** show the presence of two magnetically inequivalent P-atoms while the infrared spectrum of **12** has an absorption at 1605 cm^{-1} assignable to a non-complexed double bond. The ^1H NMR spectrum of **11** confirms the η^2-nature of the bonding of the cyclohexadiene molecule to palladium while a magnetization transfer experiment demonstrated that the inner hydrogen atoms are exchanging with each other. Similar results were obtained for the platinum complex **12** but in this case no exchange was observed.

η^1,η^1-Butadiene-platinum complexes

The structure of the platinum-butadiene complexes **6–8** is dependent upon the nature of the substituents at phosphorus in the chelating ligands. Whereas the cyclohexyl- and *tert*-butyl-substituted derivatives **7** and **8** contain η^2-bonded butadiene, the spectral evidence presented below indicates that the isopropyl substituted complex (**6**) contains an η^1,η^1-bonded butadiene moiety to give a platinacyclopentene derivative. The first indication that **6** has a different structure is the presence of a band at 1635 cm^{-1} in the infrared spectrum which is attributable to a double bond in a strained ring system.

The ^{31}P NMR spectrum differs from all the others described here: instead of an ABX spin system, a 1:4:1 triplet is observed indicating that the phosphorus atoms are equivalent and couple with the ^{195}Pt nucleus. The $^{13}C-\{^1H\}$ NMR spectrum is shown as Fig. 6.

The chemical shift for C 1 (32.4 ppm) and the value of $J_{C1,H}$ (121 Hz) are typical for an sp^3 hybridized alkyl C-atom. In addition the values for ^{195}Pt (−4654), $J_{Pt,C1}$ (605.8 Hz) and $J_{Pt,C2}$ (44.8 Hz) agree well with those obtained for related 3,4-disubstituted-platinacyclopentene derivatives [10] and the bis-η^1-allyl-platinum species $[Pt(Me_2PC_2H_4PMe_2)(\eta^1\text{-}C_3H_5)_2]$ for which values for $\delta^{195}Pt$ of −4669 ppm and for $J_{Pt,C1}$ and $J_{Pt,C2}$ of 531 Hz and 57.2 Hz have been observed [2, 14]. We have also observed [2] that the reaction of the even less sterically demanding bidentate ligand $Me_2PC_2H_4PMe_2$ with $[Pt(cod)_2]$ and butadiene leads to the formation of a divinylplatinacyclopentane derivative as the result of the coupling of two butadiene molecules at the metal.

The platinum-η^1,η^1-butadiene complex (**6**) is surprisingly inert in comparison with the complexes containing an η^2-bonded diene and no reaction is observed at room temperature with CO, CO_2 or methanol. Reaction occurs, however, with acetic acid and will be described later.

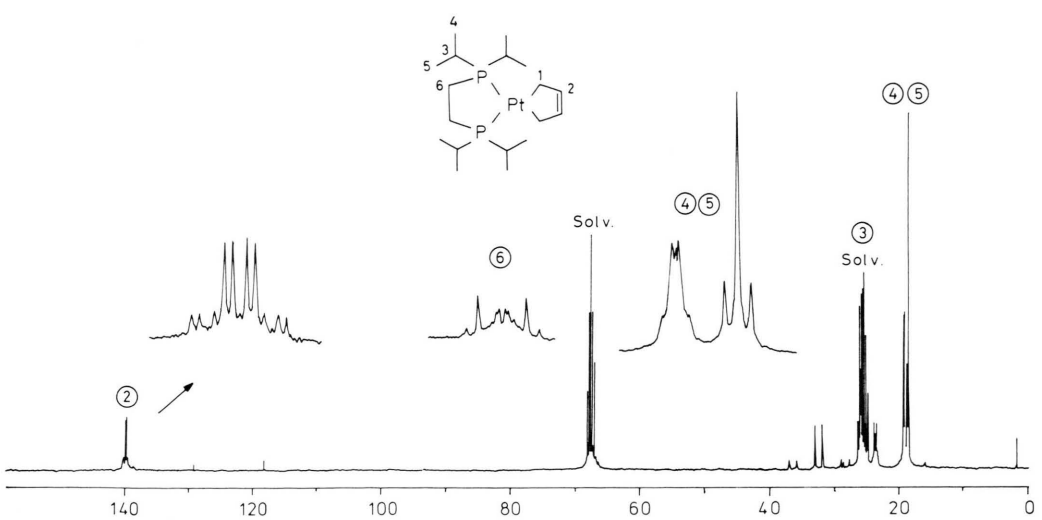


Fig. 6. $^{13}C-\{^1H\}$ NMR spectrum of $[Pt(Pr^i_2PC_2H_4PPr^i_2)(\eta^1,\eta^1\text{-}C_4H_6)]$ (**6**) (75.5 MHz, 0 °C, d_8-THF).

Experimental

Most of the organometallic compounds described below decompose at room temperature and upon exposure to air. All reactions were carried out using standard cryomat techniques and in apparatus filled with argon. The organotransition metal complexes used as starting materials were prepared by published methods: $[Ni(cod)_2]$ [15], $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)_2]$ [16], $[Pt(cod)_2]$ [17]. The bidentate phosphines were either purchased ($Cl_2PC_2H_4PCl_2$, $Me_2PC_2H_4PMe_2$, $Ph_2PC_2H_4PPh_2$, Ventron), prepared by published methods ($Cy_2PC_2H_4PCy_2$ [18]) or in the case of $Pr^i{}_2PC_2H_4PPr^i{}_2$ and $Bu^t{}_2PC_2H_4PBu^t{}_2$, which have apparently not been reported in the literature, prepared by reacting $Cl_2PC_2H_4PCl_2$ with $LiPr^i$ or $LiBu^t$ as described below.

^1H NMR spectra were measured at 80 MHz and 400 MHz using Bruker WH 80 and WH 400 instruments and the chemical shifts are relative to an external TMS sample. ^{13}C NMR spectra were measured at 25.2 MHz and 75.5 MHz using Varian XL 100 and Bruker WM 300 spectrometers and the chemical shifts measured relative to the solvent are reported relative to TMS. ^{31}P NMR spectra were measured at 32.4 MHz using a Bruker WP 80 instrument and the chemical shifts are relative to an external H_3PO_4 sample. ^{195}Pt NMR spectra were measured at 86 MHz using a Bruker WH 400 instrument and the chemical shifts are relative to $PtCl_6^{2-}$ in D_2O as an external reference.

IR spectra were measured with the FT-IR spectrometer Nicolet 7199. The mass spectra were measured with a Varian CH5 instrument. Elemental analyses were carried out in the laboratories of the firm Dornis and Kolbe, Mülheim a.d. Ruhr.

$Pr^i{}_2PC_2H_4PPr^i{}_2$

$Cl_2PC_2H_4PCl_2$ (5.03 g, 21.9 mmol) was dissolved in pentane (60 ml) and the solution cooled to −78 °C and added over 8 h to $LiPr^i$ (135 ml of a 0.65 molar pentane solution). The reaction mixture was allowed to reach room temperature and stirred overnight. The LiCl formed was filtered off, the pentane removed under vacuum and the product distilled (65−75 °C under high vacuum). Yield 1.93 g (34%).

$C_{14}H_{32}P_2$ (262.4)

Calcd	C 64.09	H 12.29	P 23.61,
Found	C 64.12	H 12.22	P 23.48.

MS: *m/z* 262 (M^+), 219 (M^+-Pr^i). ^{31}P NMR (32.4 MHz, R.T., d_8-toluene): δ 8.6. ^1H NMR (80 MHz, R.T., d_8-toluene): δ 0.8−1.2 (m, CH_3), 1.55 (m, CH, $J_{P,H}$ 125, J_{H,CH_3} 7.0 Hz), 1.46 (m, CH_2, $J_{P,H}$ 5.3 Hz).

Caution: The product inflames spontaneously in the air (probably due to the presence of impurities) and gloves should be worn-particularly when degreasing the joints of apparatus. For reasons which we have not further investigated, we experienced difficulties in regularly reproducing this preparation.

$Bu^t{}_2PC_2H_4PBu^t{}_2$

$Cl_2PC_2H_4PCl_2$ (4.88 g, 21.1 mmol) was added at −78 °C over 8 h to a solution of $LiBu^t$ in pentane (205 ml of a 0.41 mol solution). The reaction mixture was allowed to reach room temperature and stirred overnight. The LiCl was filtered off and the pentane removed under vacuum. The resulting pale yellow powder was dissolved in ethanol (50 ml) at 40 °C and the solution cooled to 0 °C whereby the product precipitated as a white powder which was isolated, washed with ethanol (2×5 ml) and dried under high vacuum. Yield 2.25 g (34%).

$C_{18}H_{40}P_2$ (318.5)

Calcd	C 67.89	H 12.66	P 19.45,
Found	C 68.09	H 12.60	P 19.34.

MS: *m/z* 318 (M^+), 261 (M^+-Bu^t), 205 ($M^+-2\ Bu^t$), 149 ($M^+-3\ Bu^t$). ^{31}P NMR (32.4 MHz, R.T., d_8-toluene): δ 35.5.

Caution: The product inflames spontaneously in the air (probably due to the presence of impurities) and gloves should be worn; particularly when degreasing the joints of the apparatus.

If the reaction is carried our at −30 °C instead of −78 °C or if the chloride is added too quickly then the main product of the reaction is the tetradentate ligand $Bu^t{}_2PC_2H_4PBu^tPBu^tC_2H_4PBu^t{}_2$ (51% yield).

$C_{28}H_{62}P_4$ (522.7)

Calcd	C 64.34	H 11.96	P 23.70,
Found	C 64.28	H 12.06	P 23.71.

MS: *m/z* 465 (M^+-Bu^t), 261, 205. ^{31}P NMR (32.4 MHz, R.T., d_6-benzene): AA′XX′ spin system $\delta_A \sim \delta_{A'}$ 34.7, $\delta_X \sim \delta_{X'}$ −5.9, ($J_{AX}+J_{AX'}$) 30.2 Hz. ^{13}C NMR (25.2 MHz, R.T., d_6-benzene): δ 31.53 (CMe_3, $J_{P,C}$ 24.2), 31.50 (CMe_3, $J_{P,C}$ 23.5), 29.0−30.5 (CH_3), 20.4−23.8 (CH_2).

$[Pd(Pr^i{}_2PC_2H_4PPr^i{}_2)(\eta^2\text{-}C_4H_6)]$ (**1**)

$[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)_2]$ (2.09 g, 9.65 mmol) was treated at −78 °C with a solution of $Pr^i{}_2PC_2H_4PPr^i{}_2$ (2.52 g, 9.61 mmol) in ether (20 ml) and butadiene (10 ml). The mixture was stirred at −10 °C for 2 days changing from a yellow suspension to a red solution. The reaction mixture was cooled to −78 °C, pentane added and the resulting yellow precipitate

collected, washed with pentane and dried under high vacuum at 0 °C. Yield 1.76 g (43%).

$C_{18}H_{38}P_2Pd$ (422.9)

Calcd	C 51.13	H 9.06	P 14.65	Pd 25.16,
Found	C 51.22	H 9.07	P 14.53	Pd 25.04.

MS: *m/z* 422 (M^+), 219 (M^+−BD/Pd). IR (KBr, R.T.): $\nu_{C:C}$ 1601 cm^{-1}. ^{31}P NMR (32.4 MHz, −80 °C, d_8-THF): AB spin system δ_A 63.4, δ_B 55.2 (J_{AB} 51 Hz). ^1H and ^{13}C NMR, see Tables I and II.

[Pd($Ph_2PC_2H_4PPh_2$)(η^2-C_4H_6)] (**4**)

This complex was prepared in 70% yield in a reaction analogous to that described above from [Pd(η^3-2-MeC_3H_4)$_2$], the bidentate phosphine and butadiene.

$C_{30}H_{30}P_2Pd$ (558.9)

Calcd	C 64.47	H 5.41	P 11.08	Pd 19.04,
Found	C 64.41	H 5.57	P 11.04	Pd 18.92.

Treatment of **4** (0.424 g, 0.83 mmol) dissolved in toluene (5 ml) with CO at 0 °C led to the absorption of 24.4 ml (1.1 mmol) and the liberation of butadiene (0.80 mmol, 96% theory; 0.04 mmol in the gas phase and 0.76 mmol in the solvent).

[Pd($Bu^t_2PC_2H_4PBu^t_2$)(η^2-C_4H_6)] (**2**)

This complex was prepared in 65% yield as an off-white solid by a procedure similar to that described above.

$C_{22}H_{46}P_2Pd$ (479.0)

Calcd	C 55.17	H 9.68	P 12.93	Pd 22.21,
Found	C 55.22	H 9.48	P 12.86	Pd 22.35.

MS: *m/z* 478 (M^+), 424 (M^+−BD), 367, 310, 261 (M^+−Bd/Pd). IR (KBr, R.T.): $\nu_{C:C}$ 1599 cm^{-1}. ^{31}P NMR (32.4 MHz, −80 °C, d_8-THF): AB spin system δ_A 82.4, δ_B 76.5 (J_{AB} 58.1 Hz). ^1H and ^{13}C NMR, see Tables I and II.

[Pd($Cy_2PC_2H_4PCy_2$)(η^2-C_4H_6)] (**3**)

[Pd($Cy_2PC_2H_4PCy_2$)(η^1-C_3H_5)$_2$] (3.49 g) was stirred in ether (25 ml) and butadiene (25 ml) for two days at 0 °C. The resulting white precipitate was isolated, washed with pentane and dried under high vacuum at 0 °C. Yield 2.72 g (81.7%).

$C_{30}H_{54}P_2Pd$ (582.7)

Calcd	C 61,78	H 9.35	P 10.62	Pd 18.24,
Found	C 61.73	H 9.52	P 10.60	Pd 18.28.

Raman (R.T.): $\nu_{C:C}$ 1604 cm^{-1}. IR (R.T., KBr): $\nu_{C:C}$ 1595 cm^{-1}. ^{31}P NMR (32.4 MHz, −30 °C, d_8-THF): AB spin system δ_A 53.7, δ_B 44.4 (J_{AB} 51.3 Hz). ^1H and ^{13}C NMR, see Tables I and II.

The same complex was prepared in 83% yield by reducing [Pd(OAc)$_2$]$_3$ with magnesium anthracene [19] in the presence of the chelating phosphine and butadiene in THF at −30 °C and identified by comparison of the ^{31}P NMR data with those shown above.

MS: *m/z* 504 (M^+−BD), 476, 398 (M^+−Pd/BD). IR (KBr, R.T.): $\nu_{C:C}$ 1600 cm^{-1}. ^{31}P NMR (32.4 MHz, −30 °C, d_8-toluene): δ 30.9. ^1H NMR (80 MHz, −30 °C, d_8-toluene): δ 7.45, 7.00 (br, Ph). ^{13}C NMR (75.5 MHz, −30 °C, d_8-toluene): δ 133.08 (br, Ph).

Treatment of **3** (1.446 g, 2.48 mmol) with H_2 at atmospheric pressure in the presence of a catalytic amount of [Ni(cod)$_2$] (16 mg) in THF (5 ml) led, over 16 h, to the absorption of 136 ml H_2 (5.6 mmol) and liberation of butane (1.01 mmol, 40.9% theory; 0.47 mmol in the gas phase and 0.55 mmol in the solvent).

Treatment of **3** (0.995 g, 1.71 mmol) with CO in THF (10 ml) at atmospheric pressure resulted, over 10 h, in the absorption of 66 ml (2.72 mmol) and the liberation of butadiene (0.84 mmol, 49.1% theory).

Treatment of **3** (1.203 g, 2.06 mmol) with $MeO_2CC{:}CCO_2Me$ (0.25 ml, 2.06 mmol) in ether (50 ml) at room temperature for 12 h resulted in the formation of a red solution which was filtered and evaporated to dryness to give 1.068 g (78% theory) of *Pd($Cy_2PC_2H_4PCy_2$)(η^2-$MeO_2CC{:}CCO_2Me$)* as a pale pink powder.

$C_{32}H_{54}O_2P_2Pd$ (638.7)

Calcd	C 57.26	H 8.18	P 8.23	Pd 15.85,
Found	C 56.56	H 7.99	P 9.40	Pd 16.16.

IR (KBr, R.T.): $\nu_{C:O}$ 1665, 1690 cm^{-1}, $\nu_{C:C}$ 1785 cm^{-1}. ^{31}P NMR (32.4 MHz, R.T., d_8-toluene): δ 64.5. ^{13}C NMR (25.5 MHz, R.T., d_8-THF): δ 122.1 (C:C, $J_{P,C}$ 72.4), 167.9 (CO_2, $J_{P,C}$ 31.1), 51.0 (CH_3).

[Pt($Cy_2PC_2H_4PCy_2$)(η^2-C_4H_6)] (**8**)

[Pt(cod)$_2$] (0.74 g, 1.80 mmol) and $Cy_2PC_2H_4PCy_2$ (0.76 g, 1.80 mmol) were suspended, at −78 °C, in ether (10 ml) and butadiene (10 ml) and stirred for 2 days at 0 °C. A greyish solid was formed which was isolated at −78 °C, washed with pentane and dried at 0 °C under high vacuum. Yield 0.67 g (50%).

$C_{30}H_{54}P_2Pd$ (671.8)

Calcd	C 53.64	H 8.10	P 9.22	Pd 29.04,
Found	C 53.66	H 8.06	P 9.28	Pd 28.86.

MS: *m/z* 671 (M^+), 617 (M^+−BD), 534, 451. IR (KBr, R.T.): $\nu_{C:C}$ 1604 cm^{-1}. ^{31}P NMR (32.4 MHz, −80 °C, d_8-THF): ABX spin system δ_A 71.3, δ_B 66.0 (J_{AB} 61.0, $J_{A,Pt}$ 3211, $J_{B,Pt}$ 3122 Hz). ^{195}Pt NMR

(86 MHz, −60 °C, d_8-THF): δ −5320 ($J_{P,Pt}$ 3170 Hz). ^1H and ^{13}C NMR, see Tables I and II.

[Pt(Bu$^t_2$PC$_2$H$_4$PBu$^t_2$)(η^2-C$_4$H$_6$)] (**7**)

This complex was prepared in 78% yield by a procedure similar to that described above.

$C_{22}H_{46}P_2Pt$ (567.6)

Calcd	C 46.55	H 8.17	P 10.91	Pt 34.37,
Found	C 47.61	H 8.01	P 10.61	Pt 33.63.

IR (KBr, R.T.): $\nu_{C:C}$ 1600 cm^{-1}. ^{31}P NMR (32.4 MHz, −30 °C, d_8-THF): ABX spin system δ_A 99.0, δ_B 97.1 (J_{AB} 72.9, $J_{A,Pt}$ 3254, $J_{B,Pt}$ 3240 Hz), see Fig. 2. ^{195}Pt NMR (86 MHz, −60 °C, d_8-THF): δ −5239 ($J_{P,Pt}$ 3219 Hz). ^1H and ^{13}C NMR, see Tables I and II and Figs 3 and 4.

[Pt(Pr$^i_2$PC$_2$H$_4$PPr$^i_2$)(η^1,η^1-C$_4$H$_6$)] (**6**)

Pt(cod)$_2$ (1.94 g, 4.71 mmol) was suspended in butadiene (10 ml) at −78 °C. Pr$^i_2$PC$_2$H$_4$PPr$^i_2$ (1.24 g, 4.73 mmol) in ether (10 ml) was added and the reaction mixture allowed to reach 0 °C and stirred for 2 days. A white precipitate was formed which was collected at 0 °C, washed with pentane and dried under high vacuum. Yield 1.81 g (75%).

$C_{18}H_{38}P_2Pt$ (511.5)

Calcd	C 42.26	H 7.49	P 12.11	Pt 38.14,
Found	C 42.39	H 7.12	P 12.04	Pt 38.34.

MS: *m/z* 511 (M^+), 457 (M^+−BD), 416, 372, 329, 287. IR (KBr, R.T.): $\nu_{C:C}$ 1638 cm^{-1}. ^{31}P NMR (32.4 MHz, −80 °C, d_8-THF): δ 71.6 ($J_{P,Pt}$ 1816). ^{195}Pt NMR (86 MHz, −30 °C, d_8-THF): δ −4654 ($J_{P,Pt}$ 1805 Hz). ^1H NMR (400 MHz, −80 °C, d_8-THF)[a]: δ 2.63 (H1, dt, $J_{1,Pt}$ 57.3, $\Sigma J_{1,P}$ 4.1), 5.83 (H2, dt, $J_{2,Pt}$ 103.6, $\Sigma J_{2,P}$ 8.2), 1.69 (H3, m, $J_{3,Pt}$ 11.8, $\Sigma J_{3,P}$ 9.8), 2.31 (H4, m, $J_{4,5}$ 7.1, $J_{4,6}$ 6.9, $\Sigma J_{4,P}$ 8.2), 1.12 (H5, dd, $J_{5,P}$ 15.3), 1.06 (H6, dd, $J_{6,P}$ 13.1). ^{13}C NMR (75.5 MHz, −30 °C, d_8-THF): δ 32.4 (C1, $J_{C,H}$ 121, $J_{P1,C}$ 91, $J_{P2,C}$ 6.1, $J_{Pt,C}$ 605.8), 139.7 (C2, $J_{C,H}$ ~144, $J_{P1,C}$ 15.1, $J_{P2,C}$ 5.4, $J_{Pt,C}$ 44.8), 18.5 (C3, $J_{C,H}$ 126±2, $J_{Pt,C}$ ~17.3), 23.6 (C4, $J_{C,H}$ 131±4), 25.9 (C5, $J_{C,H}$ 125±4, $J_{Pt,C}$ 27.5), 19.1 (C6, $J_{C,H}$ 127±2, $J_{Pt,C}$ 27.5), see Fig. 6.

[Ni(Cy$_2$PC$_2$H$_4$PCy$_2$)(η^2-C$_4$H$_6$)] (**5**)

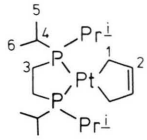
Ni(cod)$_2$ (5.21 g, 18.9 mmol) and Cy$_2$PC$_2$H$_4$PCy$_2$ (8.00 g, 18.9 mmol) were suspended in ether (50 ml) at −78 °C and butadiene (30 ml) was added. The reaction mixture was allowed to reach 0 °C and stirred for 2 days. The resulting orange suspension was cooled to −78 °C, filtered and the solid washed with cold pentane and dried under high vacuum at 0 °C. Yield 8.30 g (82%).

$C_{30}H_{54}P_2Ni$ (535.4)

Calcd	Ni 10.97	P 11.57,	
Found	Ni 10.92	P 11.61.	

MS: *m/z* 534(M^+), 480(M^+−BD), 339(M^+−BD/Ni). IR (KBr, R.T.): $\nu_{C:C}$ 1590 cm^{-1}. ^{31}P NMR (32.4 MHz, −30 °C, d_8-toluene): AB spin system δ_A 78.2, δ_B 51.3 (J_{AB} 49.9 Hz), see Fig. 5. ^1H NMR (80 MHz, R.T., d_8-toluene): δ 5.08 (m, *J* 9.0, 13.0), 3.22 (m), 3.13 (m) (C_4H_6); 1.0−2.0 (m, Cy), 1.7 (m, CH_2). ^{13}C NMR (25.2 MHz, −30 °C, d_8-toluene): δ 56.9 (C1/4), 91.7 (C2/3), 35.2 (C5), 29.31 (C6), 28.90 (C6′), 27.42 (C7), 27.42 (C7′), 26.84 (C8), 22.78 (C9), see Table II, footnote b for numbering scheme.

a



The same complex was also prepared, in 75% yield, by reacting [Ni(Cy$_2$PC$_2$H$_4$PCy$_2$)(cod)] with butadiene in ether at 0 °C.

[Pd(Cy$_2$PC$_2$H$_4$PCy$_2$)(η^2-1,3-cyclohexadiene)] (**11**)

[Pd(η^3-2-MeC$_3$H$_4$)$_2$] (1.40 g, 6.46 mmol) and Cy$_2$PC$_2$H$_4$PCy$_2$ (2.68 g, 6.34 mmol) were suspended at −78 °C in ether (5 ml) and 1,3-cyclohexadiene (5 ml) and stirred for 3 d at 0 °C. The resulting pale yellow precipitate was isolated, washed with cold pentane and dried under high vacuum at 0 °C. The complex precipitates with one molecule of cyclohexadiene. Yield 2.98 g (68%).

$C_{32}H_{56}P_2Pd \cdot C_6H_8$ (689.3)

Calcd	C 66.22	H 9.36	P 8.99	Pd 15.44,
Found	C 65.78	H 9.36	P 9.08	Pd 15.65.

^{31}P NMR (32.4 MHz, −80 °C, d_8-THF): AB spin system, δ_A 48.5, δ_B 46.5, J_{AB} 55.8 Hz. ^1H NMR (400 MHz, −80 °C, d_8-THF): δ 3.33 (H1, m, $J_{1,2}$ ~8.4 Hz), 3.62 (H2, m, $J_{2,3}$ ~5.7 Hz), 6.23 (H3, br, $J_{3,4}$ ~9.2 Hz), 4.84 (H4, br), 2.34 (H5, m), 1.45 (H6, m), 5.89, 5.79, 2.10 (free 1,3-cyclohexadiene) (numbering scheme, see **12**).

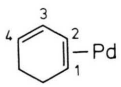
[Pt(Cy$_2$PC$_2$H$_4$PCy$_2$)(η^2-1,3-cyclohexadiene)] (**12**)

[Pt(cod)$_2$] (0.94 g, 2.29 mmol) and Cy$_2$PC$_2$H$_4$PCy$_2$ (0.97 g, 2.30 mmol) were suspended, at −78 °C, in butadiene (10 ml) and ether (10 ml) and stirred at 0 °C for 2 days. The resulting solid (the η^2-C$_4$H$_6$ complex **8**) was then stirred at 0 °C for 2 days with ether (10 ml) and 1,3-cyclohexadiene (10 ml). The product

was isolated, washed with cold pentane and dried at 0 °C under high vacuum. Yield 1.00 g (62%).

$C_{32}H_{56}P_2Pt$ (697.8)

Calcd	C 55.08	H 8.09	P 8.88	Pt 27.96,
Found	C 55.29	H 8.11	P 8.87	Pt 27.87.



MS: *m/z* 697 (M^+), 615 (M^+-Cy). IR (R.T., KBr): $\nu_{C:C}$ 1605 cm^{-1}. ^{31}P NMR (32.4 MHz, −80 °C, d_8-THF): ABX spin system, δ_A 71.4, δ_B 65.3, J_{AB} 63, $J_{A,Pt}$ 2937, $J_{B,Pt}$ 3188. ^1H NMR (400 MHz, −80 °C, d_8-THF)[a]: δ 2.96 (H2, m, $J_{1,2}$ 8.9, $J_{2,3}$ 5.9, $J_{2,P}$ 15.3), 6.32 (H3, m, $J_{3,4}$ 9.4, $J_{3,P}$ ~1.8), 4.64 (H4, m, $J_{4,5}$ ~6.3, $J_{4,6}$ ~1.7, $J_{4,P}$ 5.2).

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