NOTIZEN

η^3-Allyl-Stabilized 'Ate Complexes of Nickel, Palladium and Platinum

S. Holle, P. W. Jolly*, R. Mynott, and R. Salz
Max-Planck-Institut für Kohlenforschung,
D-4330 Mülheim-Ruhr

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η^3-Allyl Complexes, Nickelate, Palladate, Platinate Complexes

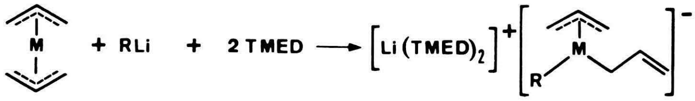
Organolithium compounds react with the bis-(η^3-allyl)metal complexes of nickel, palladium and platinum by addition to give ionic 'ate complexes in which one allyl group has been converted into the η^1-allyl form.

The ability of carbanions to act as donor ligands to metals to give the family of what is known as the 'ate complexes, *e.g.* $Na[AlEt_4]$, $K_4[Ni(C{\equiv}CR)_4]$, is well documented [1]. It is, however, only comparatively recently that K. Jonas *et al.* have isolated complexes of this type in which η^2-organic ligands interact simultaneously with the metal, *e.g.* $Li[NiMe(CH_2{:}CH_2)_2]$ [2]. As part of our investigations of the chemistry of the bis(η^3-allyl)metal complexes of nickel, palladium and platinum, we have studied their reactions with organolithium reagents: addition of a carbanion occurs and is accompanied by conversion of one of the allyl groups into the η^1-form (eq. (1)) in a manner analogous to that observed with P-donor ligands [3].

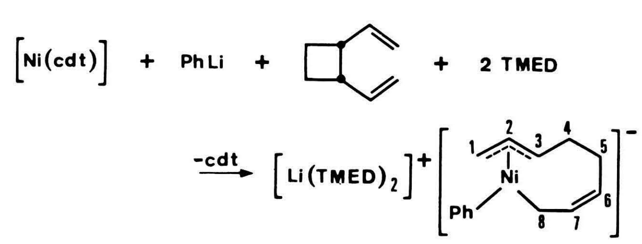
As far as we are aware these are among the first examples of 'ate complexes which also contain η^3-allyl groups. Successful reactions have been carried out with methyl-, ethyl-, vinyl- and phenyllithium while THF (or perdeutero-THF) may be used instead of tetramethylethylenediamine (TMED) as a complex partner for the lithium.

The reaction is not confined to simple bis (η^3-allyl) metal complexes and we have isolated a related species by reacting *cis*-1,2-divinylcyclobutane with zerovalent nickel in the presence of phenyllithium (eq. (2)) [4].

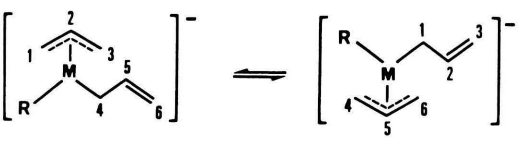
The structure of these 'ate complexes have been determined by NMR spectroscopy. Variable temperature ^{13}C NMR investigations on selected examples show that the η^1- and η^3-allyl groups undergo facile exchange (eq. (3)) in a manner similar to that observed for the $[M(\eta^1,\eta^3\text{-}C_3H_5)_2PR_3]$ complexes [3]. For example, the ^{13}C NMR spectrum of $Li[NiMe(\eta^1,\eta^3\text{-}C_3H_5)_2]$ in perdeutero-THF at



(1)



(2)



(3)

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* Reprint requests to Dr. P. W. Jolly.

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25.2 MHz consists of the expected seven signals at temperatures up to −80 °C ($\delta C_{1/3}$ 49.6, $^1J_{CH}$ 154 ± 3; δC_2 102.3, $^1J_{CH}$ 148 ± 1; $\delta C_{3/1}$ 45.1, $^1J_{CH}$ 152 ± 3; δC_4 24.2, $^1J_{CH}$ 124 ± 5; δC_5 152.5, $^1J_{CH}$ 142 ± 1; δC_6 90.3, $^1J_{CH}$ 151 ± 1; δC_{Me} −10.1, $^1J_{CH}$ 117 ± 1 Hz at −106 °C). The absorptions for C_1, C_3, C_4 and C_6 as well as those for C_2 and C_5 coalesce at *ca.* −50 °C and at 0 °C two absorptions are observed at 52.1 and 127.8 ppm.

The scope of this reaction as well as the catalytic and chemical properties of the products are being investigated further.

Experimental

$[Li(TMED)_2][PdMe(\eta^1,\eta^3\text{-}C_3H_5)_2]$

3.7 g (19.4 mmol) $[Pd(\eta^3\text{-}C_3H_5)_2]$ were dissolved in 50 ml ether at −60 °C. 28.5 ml (190 mmol) TMED and 12.7 ml (19.4 mmol) of an ethereal solution of methyllithium were added successively. A white precipitate was immediately deposited, isolated at −80 °C, washed with ether-pentane (1:5) and dried under high vacuum at −80 °C. Yield 6.0 g (70% theory).

$C_{19}H_{45}LiN_4Pd$ (443)

Calcd.	Pd 24.03	Li 1.60,
Found	Pd 24.3	Li 1.5.

$[Li(TMED)_2][NiPh(\eta^1,\eta^3\text{-}C_8H_{12})]$

5 g (22.6 mmol) [Ni(cdt)] were suspended in 100 ml ether at −78 °C. 15 ml TMED, 1.9 g (22.6 mmol) PhLi and 3.1 ml (23.0 mmol) of *cis*-1,2-divinylcyclobutane were added successively. The initial product was a yellow suspension of [NiPh(cdt)]Li [2] which reacted further at −20 °C to give the product as yellow crystals which were isolated at −30 °C, washed with ether and dried under high vacuum. Yield 7.0 g (64% theory).

$C_{26}H_{49}LiN_4Ni$ (483)

Calcd.	Ni 12.15	Li 1.45,
Found	Ni 12.1	Li 1.5.

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[1] Recent reviews include those by P. J. Davidson, M. F. Lappert, and R. Pearce, Chem. Revs. **76,** 219 (1976); R. R. Schrock and G. W. Parshall, Chem. Rev. **76,** 243 (1976); R. Taube, H. Drevs, and D. Steinborn, Z. Chem. **18,** 425 (1978).

[2] K. Jonas and C. Krüger, Angew. Chem. **92,** 513 (1980); K. Jonas, Adv. Organomet. Chem. **19,** 97 (1981).

[3] B. Henc, P. W. Jolly, R. Salz, S. Stobbe, G. Wilke, R. Benn, R. Mynott, K. Seevogel, R. Goddard, and C. Krüger, J. Organomet. Chem. **191,** 449 (1980).

[4] R. Salz, Dissertation, Ruhr-Universität Bochum 1976. $^{13}C\{^1H\}$–NMR spectrum (25.2 MHz) at −1 °C in d-THF: δC_1 49.6, $\delta C_{2,6}$ 104.6, δC_3 58.3, $\delta C_{4,5}$ 29.6, 26.2, $\delta C_{6,2}$ 100.8, δC_7 136.5, δC_8 19.3, δC_{Ph} 180.1, 141.1, 124.0, 118.0.

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