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Comparison of donor properties of *N*-heterocyclic carbenes and *N*-donors containing the 1*H*-pyridin-(2*E*)-ylidene motif*

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Abstract: IR spectroscopic and X-ray structural data of rhodium and palladium complexes of *N*-heterocyclic carbene (NHC) and 1*H*-pyridin-(2*E*)-ylidene (PYE) ligands indicate that both ligand classes exhibit similar electron-donating properties. However, catalytic application of palladium PYE complexes appears to be limited by PYE ligand loss. Density functional theory (DFT) calculations show that the Pd–C_{NHC} σ-bond is very low-lying in energy (HOMO-14 and 15, ca. –11 eV) and a π-backbonding contribution is also present, whereas the Pd-N_{PYE} σ-bond is comparatively high-lying (HOMO-9 and 10, ca. –8 eV) and the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap is also significantly less (4.0 vs. 5.6 eV). Essentially, electronegativity differences between Pd, C, and N render the Pd–N bond much more polarized and susceptible to electrophilic and nucleophilic attack and hence ligand substitution.

Keywords: density functional theory; *N*-heterocyclic carbenes; metal–ligand bonding; 1*H*-pyridin-(2*E*)-ylidenes.

INTRODUCTION

A significant attraction of molecular transition-metal chemistry is the opportunity to manipulate the properties and reactivity of a complex by modification of the ligands. There are an almost limitless number of metal–ligand combinations that are accessible from elements across the periodic table, and consequently trends are often sought to explain and predict various phenomena. Of course, the periodic table is organized to explain trends in elemental behavior and periodicity underpins much of transition-metal-based chemistry [1]. With respect to ligands, behavior can also be categorized using various criteria that reflect trends in bonding, size, and secondary interactions that are often discussed within the all-encompassing phrase of "steric and electronic properties".

To a first approximation the steric properties of a ligand can be judged from a static representation using various modeling methods, including simple plastic kits and more sophisticated computational software. Although, of course, ligand dynamics play a critical role, where metal–ligand bond lengths fluctuate as a consequence of thermal energy, in response to geometrical and oxidation-state changes, and ligand substitution. The electronic properties of ligands are perhaps more ephemeral because charge distribution in a metal–ligand bond is difficult to determine experimentally and subject to very rapid changes in comparison to the respective nuclei.

Classification of the electronic properties of a series of ligands is typically achieved using a spectroscopic probe such as the IR vibrational frequency of a metal–CO complex, ligand field strengths

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via UV–vis spectroscopy, relative ligand exchange rates (e.g., *trans*-effect), or structural determination of M–L bond lengths (e.g., *trans*-influence). Metrical data is largely restricted to a limited number of metal complex fragments in a single oxidation state with one set of co-ligands, mainly because many metal complex fragments are not amenable to the synthesis of a series of complexes or do not have a convenient spectroscopic "handle".

Consequently, more generic classifications are often used based on concepts such hard acid–soft base and the donor properties of particular ligands [2,3]. Both of these concepts are useful for identifying metal–ligand combinations that give stable complexes and complex fragments that play a role in bond formation-cleavage processes, which could also potentially be catalytic.

Herein are described two ligand classes, where spectroscopic and X-ray data suggest some commonality in electronic properties with respect to their donor strength. However, density functional theory (DFT) studies clearly indicate the deficiency in using donor strength as an indicator of reactivity, which is evidenced by comparison of palladium-catalyzed coupling reactions.

EXPERIMENTAL EVIDENCE COMPARING *N*-HETEROCYCLIC CARBENES (NHCs) AND 1*H*-PYRIDIN-(2*E*)-YLIDENE (PYE) LIGANDS

The two ligand sets that have been of recent interest to us are shown in Fig. 1. NHCs (**1**) are now well established with extensive application in metal-mediated catalysis particularly of the later transition metals [4–9]. Two distinguishing features of NHCs as ligands are their shape and electron-donating properties. The nitrogen substituents (R, Fig. 1) of NHCs project in the direction of the metal atom and are therefore a focus of ligand modification to control complex reactivity, for example, in asymmetric catalysis, and incorporation of additional donors for chelating ligand motifs is also a common strategy [5,10–14]. Electronically, NHCs are considered strong donors and supporting evidence is provided by structural, spectroscopic, and reactivity studies. For example, complexes of the type [*cis*-$Rh(CO)_2Cl(L)$] (where L is a neutral two-electron donor) have been used to classify the donating properties of ligands via IR spectroscopy, ν(CO), and NHC-containing complexes exhibit some of the lowest ν(CO) values recorded of common ligands (Table 1). New generations of NHCs and related ligands are commonly measured using the [*cis*-$Rh(CO)_2Cl(L)$] probe [15], which is then used to interpret subsequent reactivity of other metal complexes. Structurally, the *trans*-influence of NHC ligands can be judged from comparison of available X-ray data [16] on palladium complexes containing a *trans*-(L)PdCl motif (Table 2). Although not all are isostructural, the data indicates that the NHC ligand exerts a significant *trans*-influence indicative of a strong donor ligand. Other comparative evidence is provided by the selectivity in palladium-catalyzed alkylation reactions, which also indicates that NHC ligands exert a strong *trans*-labilizing effect [17].

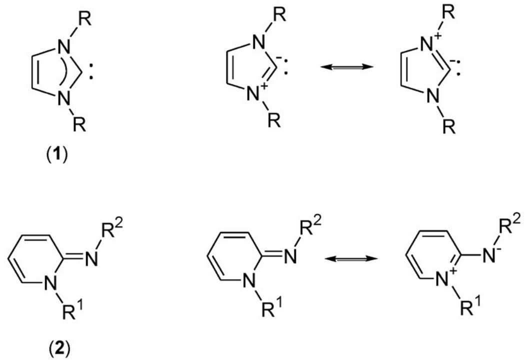


Fig. 1 NHC (**1**) and PYE (**2**) ligands and their resonance structures.

Table 1 IR spectroscopy data for [*cis*-$Rh(CO)_2Cl(L)$] complexes.

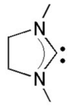
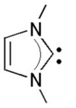
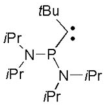
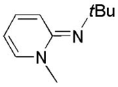
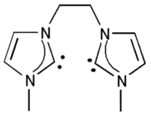
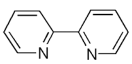
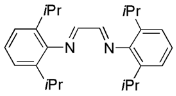
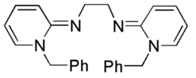
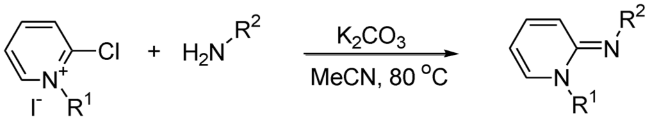
L	ν(CO)/cm^{-1}	Ref.
Pyridine	2015, 2089	[18]
PPh3	2009, 2087	[19]
PMe2Ph	2002, 2089	[19]
	1996, 2081	[20]
	2006, 2076	[21]
	1989, 2070	[22]
	1989, 2071	

Table 2 X-ray diffraction data for [*cis*-$(L_2)PdCl_2$] complexes.

L_2	d(Pd–Cl)/Å	Ref.
$Me_2NC_2H_4NMe_2$	2.304	[23]
$Ph_2PC_2H_4PPh_2$	2.358	[24]
	2.355	[25]
	2.294	[26]
	2.280	[27]
	2.320	

With respect to reactivity, there are many examples of late metal-mediated catalytic reactions which incorporate NHC and show improved performance (rate, selectivity, or lifetime) which is attributed to a strong and kinetically stable $M–C_{NHC}$ bond [4,5,9,28]. There are also stoichiometric reactions that for a series of complexes show rates for NHC-containing examples commensurate with increased metal electron density due to the strongly donating NHC ligand [29–32].

Partly with this in mind, we have recently been interested in developing a class of nitrogen ligand-based on the PYE motif (Fig. 1, **2**) [33]. Motivation was provided by the envisaged steric and electronic properties, their ease of synthesis and lack of reported coordination chemistry. PYE-type compounds can be easily prepared from reaction between an amine and pyridinium salt (eq. 1) [33,34] and the reaction is tolerant to may functional groups allowing hybrid ligand systems to be prepared. On coordination of the exocyclic nitrogen atom to a metal complex fragment, the heterocyclic *N*-substituent (R^1, Fig. 1) will point in the direction of the metal, allowing some control of the steric environment. Electronically, the PYE group was anticipated to potentially be a strong donor ligand because resonance structures can be drawn between the neutral PYE and zwitterionic pyridinium-amide (Fig. 1). Similarly, NHC can be formulated as comprising of ylide-type resonance structures (Fig. 1) [35].



(1)

Some chemistry we wished to develop stems from a simplistic idea of using PYE-type compounds as "neutral amido" ligands, where clearly the PYE-type ligand would act as both a σ- and π-donor. Due to the paucity of examples containing PYE ligands, initial chemistry explored the synthesis of several complexes incorporating the PYE motif, including chelating derivatives [33]. Metal complexes of PYE-containing compounds can be easily prepared using similar methodologies common to other two electron donors, principally substitution or cleavage of metal dimers. Specifically, the synthesis of [*cis*-$Rh(CO)_2Cl(L)$] and [*cis*-$(L_2)PdCl_2$] complexes incorporating mono-PYE and di-PYE ligands, respectively, provides spectroscopic and structural data to compare the metal–ligand bonding with other common two-electron donors. IR spectroscopic data (Table 1) shows that the CO peaks of the PYE-containing complex are similar to NHC analogs that are considered to be strongly donating. It should be noted that the use of metal complexes containing multiple carbon monoxide ligands as probes for electronic properties has been criticized, because whilst good correlations are found within a particular class of ligand, the correlation across different classes is less satisfactory [15]. An alternative complex fragment, [(Cp)Ir(CO)(L)], which contains a single CO ligand and significant space to minimize intra-ligand noncovalent interactions appears to give a more universal correlation across different ligand classes [15]. DFT calculations using this probe again show that PYE ligands appear to be amongst the strongest donating ligands known [33].

X-ray data (Table 2) shows that for the $PdCl_2$ series the *trans*-influence of the PYE ligand is less than phosphine and NHC but greater than other common NN donors. Clearly, the data is limited at this stage but the implication is that the PYE motif can be considered a strong donor. With respect to NHC, the metal-NHC bond is dominated by σ-donation, although several studies have demonstrated that both π-accepting and π-donating interactions can contribute to the overall bonding, which are dependent on ligand substitution, metal and *d*-electron count [36–38]. Notwithstanding the likely differences in metal–ligand π-bonding character the spectroscopic and structural data suggested that invoking the strong donor concept the reactivity promoted by NHC ligands may also be possible with similar PYE compounds.

REACTIVITY OF PALLADIUM NHC AND PYE COMPLEXES

Although it is well known that compounds such as phosphines and NHCs are excellent ancillary ligands for palladium-catalyzed reactions, there are also an increasing number of nitrogen-based systems derived from amines, imines, *N*-heterocycles, both monodentate and chelating, that can mediate reactions including various C–C coupling methodologies, principally Mizoroki–Heck and Suzuki–Miyaura [39–62]. In general, these classes of ligand mediate cross-coupling using aryl iodides or bromides, but for chlorides reactions are limited to activated examples [41,49,55,59]. Recently, it has also been shown that an isomer of a mono-PYE ligand can mediate the regioselective oxidative addition of aryl fluorides to nickel with rates greater than analogous NHCs and phosphine systems, which was attributed to the strongly donating *N*-ligand [63].

An opportunity would therefore appear to exist for the application of PYE-type ligands and their isomers to be applied to catalytic reactions where a strong donor ligand may be required. However, although PYE ligands possess the requisite donor abilities, and to a first approximation similar steric characteristics to NHC ligands, preliminary work does not indicate superior catalytic performance for palladium-catalyzed coupling reactions. At extended reaction times for Mizoroki–Heck and Suzuki–Miyaura palladium black precipitates from the reaction mixture and there is very low activity for substrates such as aryl chlorides where strong donating ligands are considered useful for promoting oxidative addition. In order to gain some greater insight into the comparative bonding of NHC and PYE palladium complexes DFT calculations were performed.

DFT CALCULATIONS COMPARING PALLADIUM-NHC AND -PYE BONDING

DFT calculations have been performed on the complexes shown in Fig. 2 to compare the bonding of NHC and PYE ligands coordinated to palladium, and comparison of geometrical parameters can be made with experimental data (Tables 3 and 4). Geometries were initially optimized at the BP86/SV(P) level, and vibrational frequency analyses were performed to establish that the stationary points were minima. The geometries were then re-optimized at the PBE0/def2-TZVPP level. Partial charges were calculated using the PABOON method. These calculations were performed using TURBOMOLE [64–67]. Single-point natural bond orbital (NBO) calculations were performed on the PBE0/def2-TZVPP-optimized structures using the PBE1PBE1 functional and TZVP basis set for C, H, and N and the LanL2DZ basis set and pseudopotential for Pd using Gaussian 03 (and NBO 3.1) [68,69].

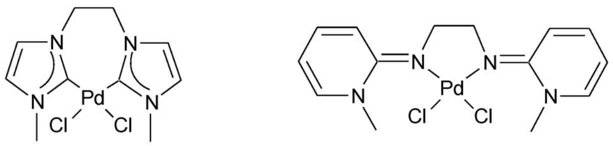


Fig. 2 Model complexes of chelating di-NHC and di-PYE ligands.

Table 3 Selected geometrical parameters and partial charges for Pd–PYE model complex.

Geometrical parameters		Partial charges		
	Dist. (Å)	Atom	PABOON	NBO
Pd-Cl1	2.285	Pd	0.3459	0.23743
Pd-Cl2	2.288	Cl1	–0.5667	–0.43059
Pd-N1	2.078	Cl2	–0.5516	–0.42642
Pd-N2	2.059	N1	–0.2138	–0.51009
		N2	–0.1514	–0.48714

Table 4 Selected geometrical parameters and partial charges for Pd–NHC model complex.

Geometrical parameters		Partial charges		
	Dist. (Å)	Atom	PABOON	NBO
Pd-Cl1	2.341	Pd	0.2713	–0.01159
Pd-Cl2	2.332	Cl1	–0.6256	–0.47920
Pd-C1	1.982	Cl2	–0.6137	–0.46749
Pd-C2	1.963	C1	–0.0426	0.33869
		C2	–0.0236	0.35986

The average Pd–Cl bond lengths in both model complexes are shorter than those found in the solid-state structures (Table 2) (0.034 Å for the PYE and 0.019 Å), likely due to the difference between the gas phase and solid state, but they show the same trends—suggesting a stronger *trans*-influence from the NHC ligand. Analysis of the average partial charges of the Pd and C atoms in the NHC complex and Pd and N atoms in the PYE complex shows, as expected based on the electronegativities of the elements, a much greater polarization of the Pd–N bond (average δ_{charge} = 0.53 PABOON, 0.74 NBO) in the PYE complex than the Pd–C bond (average δ_{charge} = 0.30 PABOON, 0.36 NBO) in the NHC complex.

Analysis of the molecular orbitals (PBE0/def2-TZVPP level) for the two complexes also highlights differences in bonding between the PYE ligands and NHCs. Selected orbitals are shown in Fig. 3. The M–N σ-bonding orbitals of the PYE complex lie at significantly higher energy (–8.0 and –8.1 eV) than the M–C σ-bonding orbitals of the NHC complex (–10.9 and –11.0 eV) suggesting an increased stability of the NHC σ-bond toward electrophiles. In addition, the lowest unoccupied molecular orbital (LUMO) of the PYE complex lies at lower energy (–1.7 eV) than that of the NHC complex (–0.4 eV), suggesting a greater stability toward nucleophilic attack. The extent of M–L back-bonding in these complexes can be estimated by analysis of the Pd "lone pair" orbitals in the NBO calculations, which hold the 8 *d*-electrons in this model. In the PYE complex, the average occupation of these Pd orbitals is 1.984 electrons and does not vary a great deal between the four orbitals (although one is a little lower than average at 1.977 electrons). In contrast, in the NHC complex one of the Pd lone pairs has a much

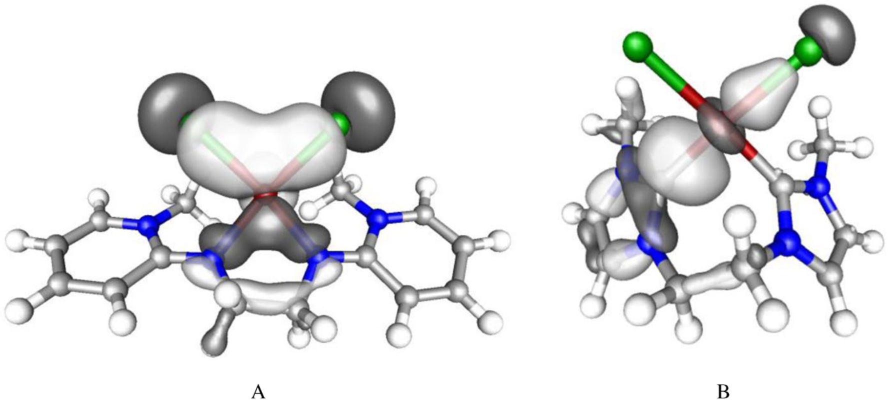


Fig. 3 Selected molecular orbitals (PBE0/def2-TZVPP) for the model Pd complexes. The HOMO of the Pd–PYE complex lies at –5.71651 eV and the Pd–NHC HOMO lies at –5.96277 eV. (A) Pd–PYE complex HOMO-9 (–7.998 eV). A similar M–N σ-bonding orbital is found at –8.130 eV. (B) Pd–NHC complex HOMO-14 (–10.929 eV). A similar orbital involving the other M–C σ-bonding orbital is found at –11.013 eV.

lower occupation of 1.920 electrons. This is involved in back donation to the carbene and suggests that there is some π-back donation in this complex, whereas little π-back donation is suggested in the PYE system as would be expected.

Essentially, the greater spread of orbital energies for the Pd–NHC complex in comparison to the Pd–PYE is indicative of greater metal–ligand orbital interaction and stronger bonding.

Pd(II)–NHC bonding has been examined previously for mono-NHC complexes [70,71]. Essentially, strong donation by NHC ligands originates from the carbon-based σ-orbital in the plane of the heterocycle and calculations suggest that there is also a π-bonding component in metal complexes orthogonal to the plane. For Pd(II), the contribution is estimated to be ca. 10–15 % with the vast majority ca. 95 % attributable to π-acidity. The kinetic stability of Pd–NHC complexes has been attributed to the low-lying Pd–C σ-bond, although it should be noted that palladium(0) bis mono-NHC complexes are known to dissociate an NHC ligand [32,72,73].

CONCLUDING REMARKS

Although both NHC and PYE ligands can be classified as strong donors as judged by spectroscopy, there are limitations with respect to the use of PYE ligands as kinetically stable ancillary ligands in palladium-catalyzed chemistry. Palladium-NHC chemistry is characterized by a kinetically robust Pd–C_{NHC} bond that is a consequence of very low-lying Pd–NHC σ-bond and small yet sufficient π-acidity to mediate formal oxidation state changes of catalytic intermediates. Essentially, the very small electronegativity difference between palladium and carbon in the Pd–NHC bond renders the bond almost entirely covalent and therefore resistant to electrophilic and nucleophilic attack. In contrast, Pd–PYE bonding is characterized by a high-lying Pd–PYE σ-bond and significantly more ionic character because of the greater electronegativity difference between palladium and nitrogen. The lack of π-acidity also accentuates the polarization of the Pd–N bond. Consequently, the Pd–PYE bond is susceptible to electrophilic and nucleophilic attack resulting in PYE ligand loss or substitution during a catalytic cycle. However, work has shown that in stoichiometric reactions PYE-type compounds do indeed engender high metal electron density that can promote selective and rapid oxidative addition [63]. A recent theoretical study compared oxidative addition, transmetallation, and reductive elimination steps for the Suzuki–Miyaura reaction using chelating phosphine, imine, and amine ligands [44]. This study showed that the activation energy for oxidative addition was lowest for imines but that nitrogen ligands gave much higher activation energies for reductive elimination, which would be commensurate with low π-acidity. In this respect, PYE ligands could perhaps be considered too strongly donating, resulting in a prohibitively high activation energy for reductive elimination. A potential strategy would be to incorporate a PYE motif as a hemilabile moiety in a chelating ligand that can promote oxidative addition when required.

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