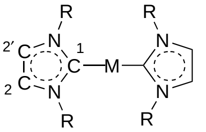
An experimental and theoretical investigation of the electronic structure of Pd and Pt bis(carbene) complexes

Jennifer C. Green,*[a] Robert G. Scurr,[a] Polly L. Arnold[b] and F. Geoffrey N. Cloke[b]

[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR*
[b] *School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UK BN1 9QJ*

Photoelectron spectra and density functional calculations are reported for $M(CN_2R_2C_2H_2)_2$ (M = Pd, Pt); bonding occurs predominantly through σ donation from the carbene lone pairs into a metal (d_{z^2} + s) hybrid; the corresponding (d_{z^2} − s) is destabilised with respect to the other metal orbitals; there is little evidence for π bonding and the carbene π orbitals are essentially unperturbed on complexation.

Isolation by Arduengo of stable carbenes by deprotonation of imidazolium salts[1] has opened up new routes to the synthesis of transition-metal carbene compounds.[2–6] The bis(carbenes) of the group 10 metals, Ni, Pd and Pt, are particularly striking being examples of stable neutral two-coordinate complexes. Together with the isoelectronic complexes of the group 11 metal ions, Cu^+, Ag^+ and Au^+, they show linear coordination,[5,6] which is common for d^{10} metal ions. Though the bonding in the case of the monocations is likely to be predominantly σ donation from the nucleophilic carbene carbons, with the group 10 metals the question arises as to the degree of π-back donation from the metal to the carbene.



1 M = Pd, R = Bu^t **3** M = Pd, R = H
2 M = Pt, R = Bu^t **4** M = Pt, R = H

Crystal structure determinations on $M(CN_2Bu^t_2C_2H_2)_2$ (M = Pd **1**, Pt **2**) show the molecular framework to approximate to D_{2d} symmetry with the two rings orthogonal to one another.[7] We consequently classify the molecular orbitals (MO) in this point group. It is also helpful to define their symmetry with respect to the local symmetry at the metal, $D_{\infty h}$. The primary bonding orbital (a_1 or σ_g) is expected to be a linear combination of the carbene lone pairs and a metal (d_{z^2} + s) hybrid directed towards the ligands [Fig. 1(*a*)]. Interaction of the out-of-phase lone pair combination (b_2 or σ_u) with the metal p_z orbital is expected to be less favourable on both energy and overlap grounds [Fig. 1(*b*)]. The metal orbitals which are possible candidates for π-back donation to the ligands are the d_{xz} and d_{yz} orbitals (e or π_g). They can interact with ligand π_1, π_3 or π_5 orbitals. The ligand π_2 and π_4 orbitals give linear combinations b_1 and a_2 in symmetry (δ and ϕ respectively). The remaining d orbitals which are δ in symmetry (d_{xy} b_2 and $d_{x^2-y^2}$ b_1) are expected to have minimal interaction with the ligands. The ten metal electrons will occupy four metal d orbitals and a d_{z^2} − s hybrid [Fig. 1(*c*)].

We have investigated the bonding in these compounds by a combination of photoelectron (PE) spectroscopy and calculations using density functional theory (DFT).

He I and II PE spectra were obtained for **1** and **2**.† The Ni compound was insufficiently volatile for PE spectroscopy. The spectra are shown in Fig. 2 and vertical ionisation energies (E_i) are given in Table 1 together with those of $(CN_2Bu^t_2C_2H_2)$.[8]

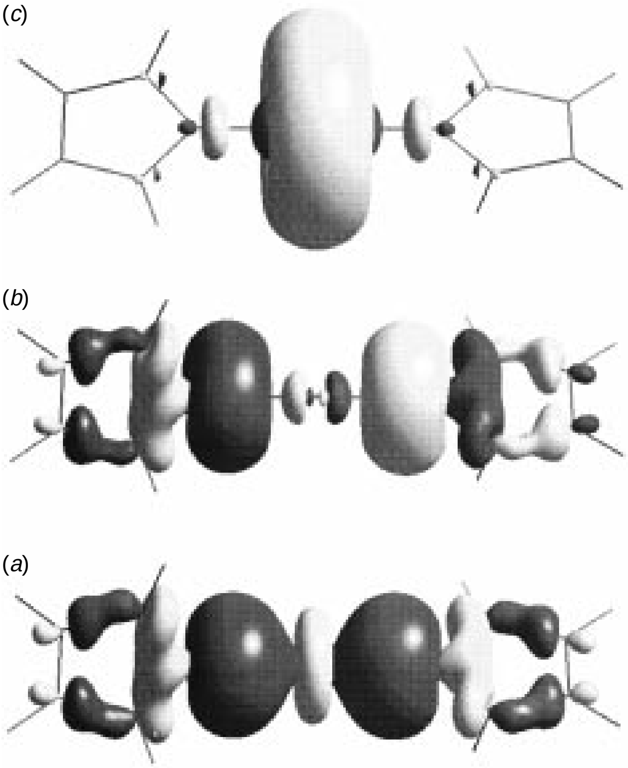


Fig. 1 The principal σ orbitals of **3** and **4**: (*a*) σ_g bonding orbital (*b*) σ_u bonding orbital (*c*) s–d_{z^2} hybrid (surfaces were generated using the Cerius2 package of MSI)

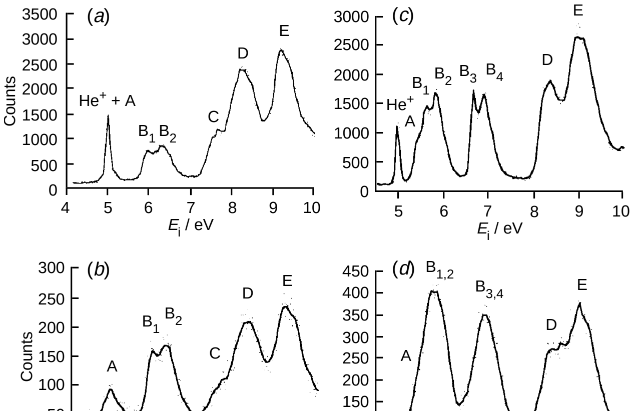


Fig. 2 He I (*a*) and He II (*b*) PE spectra of **1** and He I (*c*) and He II (*d*) PE spectra of **2**

Table 1 Experimental E_is for **1** and **2** and free ligand **5**, calculated E_is for **3** and **4** and ion state assignments

Band	E_i **1**	Calc E_i **3**	Assignment		Orbital type[a]		E_i **2**	Calc E_i **4**	Assignment		Orbital type[a]		E_i **5**	Assignment
A	5.00	6.4	$^2A_1$	σ_g	$z^2 - s$	nb	5.5	6.8	$^2A_1$	σ_g	$z^2 - s$	nb		
B_1	5.96	7.3	^2E	π	xz, yz	nb	5.64	7.2	$J = 5/2$	δ	$x^2 - y^2, xy$	nb		
B_2	6.36	7.5	$^2B_1, {}^2B_2$	δ	$x^2 - y^2, xy$	nb	5.84	7.2	$J = 3/2$	π	xz, yz	nb		
B_3							6.67	7.2	$J = 1/2$	π	xz, yz	nb		
B_4							6.93	7.2	$J = 3/2$	δ	$x^2 - y^2, xy$	nb		
C	7.36	9.5	$^2B_2$	σ_u	lig. σ	b					lig. σ	b	7.68	σ
D	8.25	8.8	^2E	π	lig. π_3	nb	8.34	8.9	^2E	π	lig. π_3	nb	8.22	π_3
E	9.17	10.3	$^2A_2, {}^2B_1$	δ	lig π_2	nb	8.98	9.8	$^2B_2$	σ_u	lig. π_2	nb	9.24	π_2
								10.3	$^2A_2, {}^2B_1$	δ				
		11.7	$^2A_1$	σ_g	$z^2 + s +$ lig. σ	b		13.0	$^2A_1$	σ_g	$z^2 + s +$ lig. σ	b		

[*] nb = non-bonding, b = bonding, lig. = ligand.

The spectrum of **1** shows one low lying ionisation band, A; in the He I spectrum, the first band lies under the sharp He self-ionisation band (He ionised by He II radiation) but is readily apparent in the He II spectrum. This is followed by a more complex band structure B. Intensity changes between the He I and He II spectra indicate that bands A and B arise from ionisation of metal localised electrons. Band A is assigned ionisation from the $d_{z^2} - s$ hybrid and band B to ionisation from the four Pd d orbitals. Bands C, D and E correspond closely in position to the first three ionisation bands of the free carbene (Table 1).[8] The band profile, however, differs in that band C is lower in intensity in the complex and bands D and E are less resolved. In the free carbene the first PE band is associated with ionisation of the carbene lone pair. The change in band profile on complexing is consistent with stabilisation of the σ_g linear combination of the lone pairs in the complex. Band C in the Pd complex is assigned to ionisation of the σ_u orbital. The lack of shift or apparent splitting of bands D and E suggest negligible metal–ligand π interaction. From the spectrum there is no direct evidence of the location of the σ_g ionisation band.

The PE spectrum of **2** is assigned by comparison with that of **1**. The first band A, the σ_g ionisation lies at higher energy. Band B, assigned to the d ionisations, shows a significantly greater spread of E_i. Given an effective linear potential at Pt, the splitting is attributable to spin–orbit (SO) coupling, that of the δ orbitals, giving $J = 5/2$ and 3/2, being twice that of the π orbitals, giving $J = 3/2$ and 1/2. In the absence of SO coupling the π and δ E_is would be *ca.* 6.2 eV, closely similar to those found for Pd. This suggests that the larger E_i for band A is due to the relativistic stabilisation of the Pt 6s orbital. Band C of the Pd spectrum has no analogue in the spectrum of **2**. We infer that the σ_u orbital is more tightly bound compared with the π ligand bands which again give rise to bands D and E with similar E_is to the free ligand. There is no direct evidence for the σ_u and σ_g ionisation bands but the changed intensities of bands D and E compared with the Pd spectrum suggests that the σ_u ionisation may lie under band E.

DFT calculations have been carried out for $M(CN_2H_2C_2H_2)_2$ (M = Pd **3**, Pt **4**), assuming D_{2d} symmetry.‡ The geometries were optimised for the ground-state molecules. The distances and angles thus found are compared with those from the crystal structures of **1** and **2**.§ Ionisation energies were calculated both by Slater's transition-state method[14] and by carrying out calculations for the molecular ions $\mathbf{3}^+$ and $\mathbf{4}^+$ in the ion ground state and the first eight excited states using the optimised geometry for the molecule. Though both methods gave a similar E_i pattern the values by the former method were more satisfactory. They are compared with the E_is measured for **1** and **2** in Table 1. The presence of the *tert*-butyl groups in the measured compounds means that precise agreement with theory is not anticipated; alkyl substitution is expected to lower the E_i of a molecule. Good agreement between the pattern of calculated and experimental E_i confirms the assignment of bands given above. Comparing **3** with **1** suggests that the calculation overestimates the ionisation energy of the σ_u orbital. The calculations also suggest that for both **1** and **2** the σ_g bonding ionisation lies under the main band which commences at 10 eV, and that for **2** the σ_u ionisation lies in the envelope of bands D and E.

The combined weight of the experimental and theoretical evidence suggests that the bis(carbenes) of Pd and Pt have metal–ligand σ bonds and π bonding is minimal.

Footnotes and References

* E-mail. jennifer.green@icl.ox.ac.uk

† PE spectra were measured using a PES Laboratories 0078 spectrometer and calibrated with He, Xe and N_2

‡ Calculations were performed using the density functional methods of the Amsterdam Density Functional (ADF) code Version 2.0.1.[9] The basis set used triple-ζ accuracy sets of Slater orbitals with a single polarisation function added to main group atoms, 2p on H, 3d on C and N. Cores of the atoms were frozen (C, 1s; N, 1s; Pd, 4p; Pt, 5p), those of Pd and Pt being relativistic. Vosko, Wilk and Nusair's local exchange correlation potential[10] was employed with non-local exchange corrections by Becke[11] and non-local correlation corrections by Perdew.[12,13]

§ Experimental bond lengths for **1** and **2** and calculated bond lengths for **3** and **4** (Å)

	1	**2**	**3**	**4**
M–C(1)	2.041(6)	1.965(12)	2.08	2.00
C(1)–N	1.361(6)	1.384(11)	1.39	1.40
N–C(2)	1.374(9)	1.397(13)	1.41	1.41
C(2)–C(2′)	1.36(2)	1.31(2)	1.37	1.37

1 A. J. Arduengo III, R. R. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.
2 M. Regitz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 725.
3 N. Kuhn, T. Kratz, R. Boese and R. Blaeser, *J. Organomet. Chem.*, 1994, **470**, C8.
4 K. Öfele, W. A. Herrmann, D. Mihalios, M. Elison, E. Herdweck, W. Scherer and J. Mink, *J. Organomet. Chem.*, 1993, **459**, 177.
5 A. J. Arduengo III, S. G. Gamper, J. C. Calabrese and F. Davidson, *J. Am. Chem. Soc.*, 1994, **116**, 4391.
6 A. J. Arduengo III, H. V. Raisaka Dias, J. C. Calabrese and F. Davidson, *Organometallics*, 1993, **12**, 3405.
7 P. L. Arnold, F. G. N. Cloke, T. Geldbach and P. B. Hitchcock, manuscript in preparation.
8 A. J. Arduengo III, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. Jones, M. Wagner and R. West, *J. Am. Chem. Soc.*, 1994, **116**, 6641.
9 B. te Velde and E. J. Baerends, *J. Comput. Phys.*, 1992, **99**, 84.
10 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.
11 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 2398.
12 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
13 J. P. Perdew, *Phys. Rev. B*, 1986, **34**, 7046.
14 J. S. Slater, *The Calculation of Molecular Orbitals*, Wiley, New York, 1979.

Received in Cambridge, UK, 18th July 1997; 7/05157C