Phosphorus Lone Pairs

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Charge Density Distribution in a Metallaphosphane**

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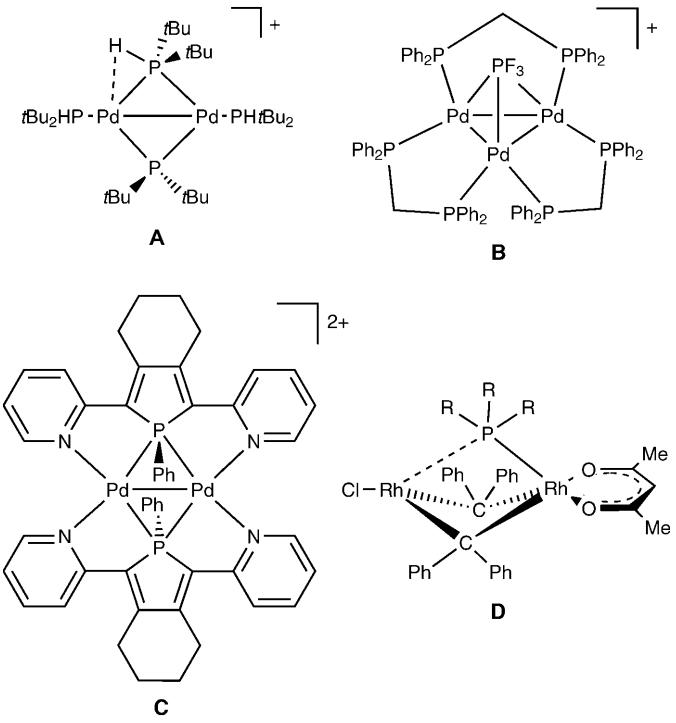
Dedicated to Professor S. S. Krishnamurthy on the occasion of his 70th birthday

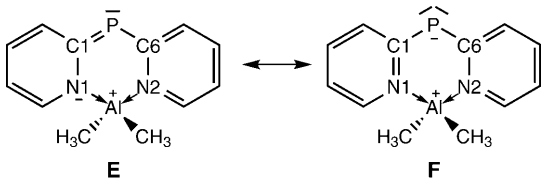
Tertiary phosphanes are unequivocally the most important donor ligands in catalytically active d-block organometallics.[1] The majority of the employed PR_3 phosphanes can be regarded as terminal two-electron donors to a single metal atom, even in multimetallic arrays. The most common coordination mode for R_2P^- phosphanides,[2] namely μ bridging, was only recently found for phosphanes.[3] The originally isolated four-electron-donating complexes accommodate a phosphorus atom bridging a Pd–Pd bond and donating an additional charge to one metal atom, either by a P–H[4] (**A**; see Scheme 1) or a P–C bond (**B**).[5] Similar to the well-established μ_3-bridging two-electron-donating CO, the tertiary phosphane PF_3 is located symmetrically above a palladium triangle[6] (**B**). Two phosphole ligands bridge a Pd–Pd bond in a dicationic complex akin to **C** in Scheme 1.[7] PMe_3 was initially found as an asymmetric bridge (**D**; Scheme 1) in a dinuclear rhodium complex.[8]

Herein we present the experimental and theoretical charge density of $[Me_2Al(\mu\text{-}Py)_2P]$ (**1**; Py = 2-pyridyl) and the structure of the μ-bridging $HPPy_2$ phosphane coordinated to two unsupported pentacarbonyltungsten moieties in the dinuclear complex $[\{(OC)_5W\}_2PPy_2(H)]$ (**2**). The results provide evidence for both Py_2P^- and $HPPy_2$ mimicking four-electron donors.

The first preparation of $[Me_2Al(\mu\text{-}Py)_2P]$ (**1**), which contains an unusual divalent phosphorus(III) atom and a Me_2Al^+ moiety[9] coordinated to both pyridyl ring nitrogen atoms, poses the question whether the phosphorus atom should be regarded a two-electron (**E**; see Scheme 2) or a four-electron donor (**F**; Scheme 2). The Py_2P^- anion easily



Scheme 1. Various μ-coordination modes of phosphanes.



Scheme 2. Two canonical forms to rationalize the bonding in $[Me_2Al(\mu\text{-}Py)_2P]$ (**1**).

adopts a non-conjugated butterfly conformation in various metal complexes[10] and is not restricted to the planar arrangement as found in the Py_2CH^-[11] or the Py_2N^- anion.[12] Remarkably, the phosphanide is stable even after dual P=N bond cleavage in $Py_2P(NHSiMe_3)(NSiMe_3)$ with organometallic moieties.[13] Computational studies suggested electronic depletion at the phosphorus atom in **1**, which therefore makes it a poor Lewis base to any organometallic moiety.[14] However, the parent Py_2P^- anion exhibits a μ-bridging phosphorus atom in the complex cation

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$[\{Cp(CO)_2Fe\}_2\{(\mu\text{-}P)Py_2\}]^+$ and a σ- and π-donating phosphorus atom in dimeric $[(pmdeta)Cs\{(\mu\text{-}PyP)Py\}]_2$ (pmdeta = pentamethyldiethylenetriamine), which suggests charge-density accumulation at the phosphorus atom.[15]

To elucidate the bonding situation at the phosphorus atom in $[Me_2Al(\mu\text{-}Py)_2P]$ (**1**), we determined the charge density distribution experimentally and theoretically.[16] The experimental density is based on a multipole refinement[17] of 100 K high-resolution ($(\sin\theta/\lambda)_{max} = 1.15$ Å^{-1}) X-ray data employing XD.[18] The theoretical results were obtained at the B3LYP/def2-TZVP level of theory with Turbomole.[19] The results of the topological analyses[20] are presented in Table 1 in terms of the charge density $\rho(\mathbf{r})$ and the Laplacian $\nabla^2\rho(\mathbf{r})$ according to Bader's quantum theory of atoms in molecules (QTAIM).[21]

Table 1: Topology of selected bonds in $[Me_2Al(\mu\text{-}Py)_2P]$ (**1**).[a]

A–B	d(A–B) [Å]	d(A–BCP) [Å]	d(BCP–B) [Å]	$\rho(\mathbf{r}_{BCP})$ [Å^{-3}]	$\nabla^2\rho(\mathbf{r}_{BCP})$ [e Å^{-5}]
P–C1	1.793	0.823	0.970	1.13(1)	−4.83(3)
	1.795	*0.690*	*1.105*	*1.07*	*1.30*
P–C6	1.787	0.831	0.957	1.25(1)	−6.25(3)
	1.795	*0.690*	*1.105*	*1.07*	*1.28*
N1–C1	1.363	0.827	0.537	2.27(1)	−24.32(5)
	1.370	*0.852*	*0.511*	*2.17*	*−24.26*
Al–N1	1.930	0.830	1.100	0.54(1)	5.96(2)
	1.955	*0.798*	*1.157*	*0.45*	*7.96*
Al–N2	1.926	0.829	1.097	0.49(1)	6.60(2)
	1.955	*0.798*	*1.157*	*0.45*	*7.96*

[a] d(A–B): distance between atoms A and B along the bond path; d(A–BCP), d(BCP–B): distances between the BCP and the atoms A and B, respectively; $\rho(\mathbf{r}_{BCP})$: charge density at the BCP; $\nabla^2\rho(\mathbf{r}_{BCP})$: Laplacian at the BCP. All the theoretical values (in italics) are obtained by B3LYP/def2-TZVP calculations.

All the bond critical points (BCPs) are shifted towards the more electropositive atoms. The theoretical BCP displacements are more pronounced than the experimental values (for example d(P–BCP): experimental 0.823/0.831 Å; theoretical *0.690*/*0.690* Å). As a consequence, the values of the electron density at the BCPs differ slightly for the theoretical and experimental study. This effect is well-known for combined experimental and theoretical studies.[22] The value of the Laplacian at the P–C BCP is slightly positive for the theoretical calculations ($\nabla^2\rho = +1.30/+1.28$ e Å^{-5}) and negative for the experimental results ($\nabla^2\rho = -4.83/-6.25$ e Å^{-5}). However, the contour plots show overall similarity to each other and to the two P–Ph single bonds in $[(Et_2O)Li\{Ph_2P\text{-}(CHPy)(NSiMe_3)\}]$, and thus do not indicate pronounced double bonding (Figure 1).[23] This result is the first evidence against conjugation and thus against a distinct contribution of form **E** in Scheme 2, despite the short bond path of 1.79 Å, which might erroneously be taken as an indicator for P=C double bond character (P–C in phosphabenzene[24] circa 1.74 Å and circa 1.79 Å in phospholides[25]).

The Al–N bonds are pronouncedly ionic owing to the positive Laplacian at the BCP of circa 6 e Å^{-5} and by the QTAIM charge separations (exp./theor.:[26] −1.21/*−1.11* and −1.15/*−1.09* e for the two nitrogen atoms and +2.04/*+2.30* e for Al). The charge of the phosphorus atom of +0.56 e

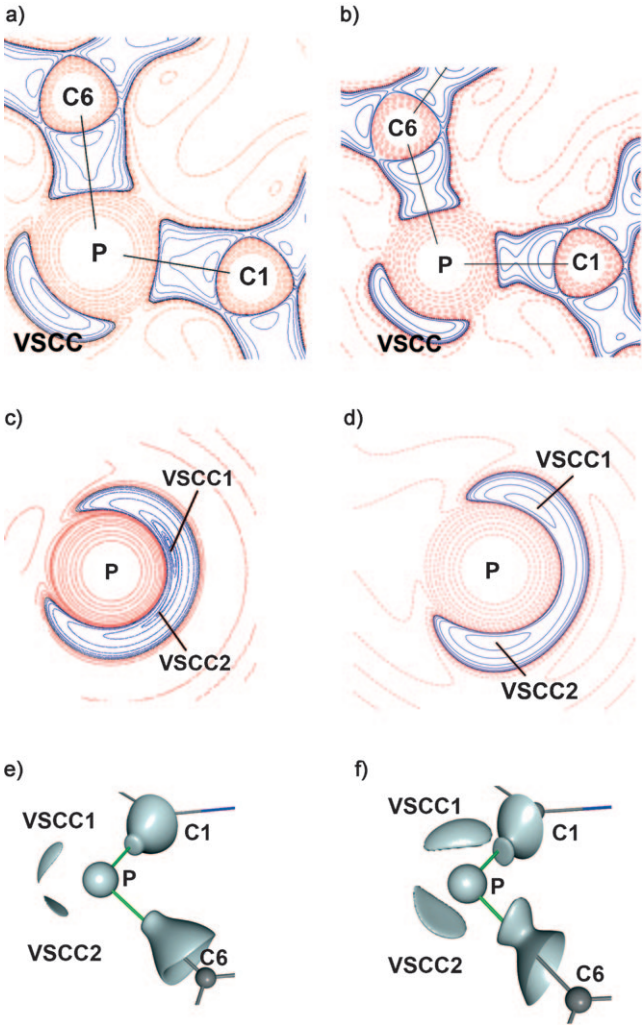

Figure 1. Theoretically (left) and experimentally (right) obtained distributions of $\nabla^2\rho$: a,b) In the C1-P-C6 plane and c,d) in the plane defined by phosphorus and the two nonbonding VSCCs in $[Me_2Al(\mu\text{-}Py)_2P]$ (**1**). Charge concentrations (blue lines) refer to negative values of $\nabla^2\rho(\mathbf{r})$, charge depletions (red lines) to positive values. e,f) Isosurface representation of $\nabla^2\rho(\mathbf{r})$ around P1 at the −4.9 e Å^{-5} (e) and −4.0 e Å^{-5} level (f), indicating the two lone pairs in the non-bonding region.

indicates electronic depletion. In the non-bonding region, one VSCC above and one below the molecular plane was detected close to the phosphorus atom (exp.: −5.58/−5.06 e Å^{-5}; theor.: *−4.74*/*−5.32* e Å^{-5}; see Figure 1). Third- and fourth-order Gram–Charlier anharmonic motion parameters for the phosphorus atom and third-order parameters for the aluminum atom in **1** are included in the refinement.[27] Only with this procedure does the residual density distribution become flat and featureless in the whole unit cell (as indicated by the parabolic shape of the black dots in Figure 2).[28] The residual density was calculated on a 106 × 86 × 141 grid.

In accordance with the small reduction of the R value from 1.64 % to 1.55 %, the decrease in e_{gross} is also small, as is the increase in $d^f(0)$ from 2.6710 to 2.6730. Figure 2 shows that the distinct shoulders vanish when anharmonic motion is taken into account. In consequence, the residual density distribution becomes flat ($\Delta\rho_0 = 0.57$ e Å^{-3} decreases to $\Delta\rho_0 =$

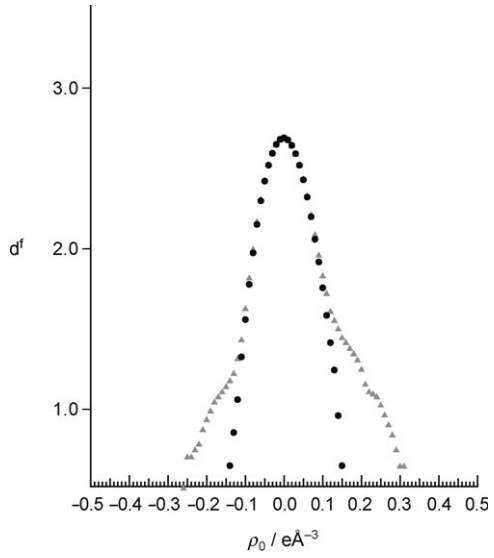

Figure 2. Residual density distribution ρ_0 in the whole unit cell of **1** prior to (gray triangles) and after (black dots) inclusion of anharmonic motion. d^f = fractal dimension.

0.30 e Å^{-3}) and featureless, as indicated by the parabolic shape, which corresponds to a Gaussian distribution of residuals.

In QTAIM, the VSCCs are interpreted as indicating the lone pairs located in the distorted phosphorous sp^3 orbitals, although the VSCC1-P-VSCC2 angle of 152.08° is substantially wider than the tetrahedral angle. This orientation of the VSCCs may be anticipated from the symmetrically bridging position of the Py_2P^- phosphanide to two iron atoms in $[\{Cp(CO)_2Fe\}_2\{(\mu\text{-}P)Py_2\}]^+$ (Fe1-P-Fe2 120.49(7)°) above and below the plane of the anion,[15] but with the metallaphosphane $[Me_2Al(\mu\text{-}Py)_2P]$ (**1**), this finding is remarkable. The narrow VSCC1-P-VSCC2 angle of about 70° in theory is found for different basis sets and functionals (see the Supporting Information).

From simple electronegativity considerations, it might be anticipated that the replacement of the phenyl groups in Ph_2P^- by the better π-accepting pyridyl groups would result in a shift of negative charge from the phosphorus atom to the ring nitrogen atoms, thereby inducing pronounced P–C_{ipso} double-bond character (**E**; Scheme 2). Coordination of the metal to the ring nitrogen atom would even support this effect. In contrast with this consideration, the experimentally determined non-bonding VSCCs at the phosphorus atom suggest the presence of two lone pairs reminiscent to **F** in Scheme 2, which is in accordance with the theoretical results.

The orientation of the phosphorus atom lone pairs seems to be suitable for accepting two $\{(L_n)M\}$ Lewis acidic organometallic residues. By analogy, if the density in the Py_2P^- phosphanide was suitable to enable the μ-bridging coordination mode[14] in $[\{Cp(CO)_2Fe\}_2\{(\mu\text{-}P)Py_2\}]^+$, compound **1** might as well serve as a μ-bridging phosphane in a dinuclear complex. To test this hypothesis and the Lewis basicity of **1** synthetically, we embarked upon the preparation of a dinuclear organometallic metallaphosphane complex. We selected $[W(CO)_5(thf)]$ as the appropriate starting material because the THF molecule can easily be replaced by other Lewis bases and the remaining $\{W(CO)_5\}$ moiety should be soft enough to suite the soft metallaphosphane.[29] Phosphanides bridging two tungsten atoms are known in anionic complexes such as $[\{(CO)_5W\}_2\{(\mu\text{-}P)H_2\}]^-$[30] and $[\{(CO)_5W\}_2\{(\mu\text{-}P)(C_6F_5)_2\}]^-$.[31]

Compound **1** was thus reacted with $[W(CO)_5(thf)]$. Pale yellow crystals were grown from the reaction mixture within two weeks at room temperature. Surprisingly, the X-ray structure analysis revealed their composition to be $[\{(OC)_5W\}_2(\mu\text{-}P)Py_2(H)]$ (**2**; Figure 3). In the course of the reaction, the Me_2Al^+ moiety was lost and replaced by a proton to generate the μ-bridging $PPy_2(H)$ phosphane, akin to an N-protonated phosphanide. Side reactions with air and water can be excluded because the reaction was repeated several times under strict inert gas conditions. We assume that ether cleavage reactions by C–H activation of THF by the Me_2Al^+ cation gives protons, insoluble aluminum alkoxides, and enolates precipitating from the solution. Further investigations to elucidate the nature of the side products are under way.

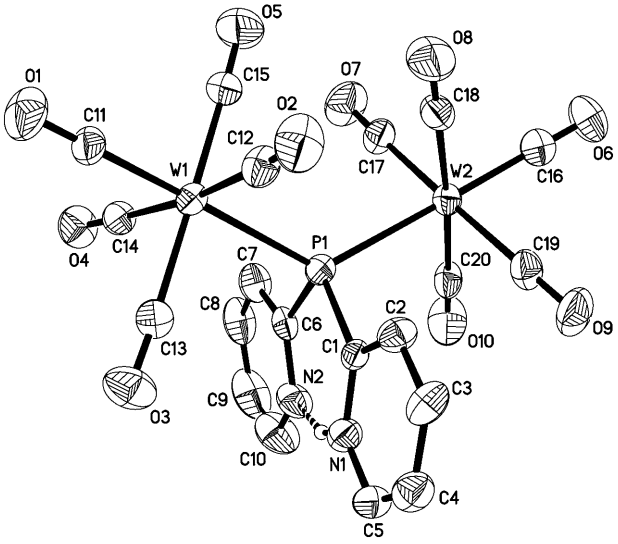

Figure 3. The structure of $[\{(OC)_5W\}_2(\mu\text{-}P)Py_2(H)]$ (**2**) in the solid state; ellipsoids set at the 50% probability level. Only the freely refined N–H···N bonded hydrogen atom is depicted; all other hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.843(5), P1–C6 1.843(5), P1–W1 2.583(1), P1–W2 2.588(1), N1–H1 0.88(6), N2···H1 1.73(6); C1-P1-C6 103.1(2), W1-P1-W2 126.9 (1).

In complex **2**, the hydrogen atom of the secondary phosphane is bonded to one ring nitrogen atom. The position of the N–H···N hydrogen atom was taken from the Fourier difference map and refined freely. H1 is unambiguously located at N1, which seems surprising as in the parent dipyridylphosphane $HPPy_2$ the hydrogen atom is bonded to the phosphorus atom (^{31}P NMR: $^1J_{(P,H)} = 225$ Hz; IR, ν_s(P–H): $\tilde{\nu} = 2312$ cm^{-1}),[32] and to date only diacylphosphanes show keto–enol tautomerism in solution.[33] The symmetrical coordination of the two tungsten atoms to the central phosphorus atom is in geometrical accordance with the two lone pairs of

form **E** in Scheme 2. The P–W distances are almost equal to those in $[\{(CO)_5W\}_2\{(\mu\text{-}P)H_2\}]^-$.[24] The extra negative charge of the H_2P^- bridge compared to the neutral $PPy_2(H)$ in **2** does not appear to lead to closer contacts to the Lewis acidic tungsten atoms. Only the two electron-withdrawing F_5C_6 groups in the bridging $(F_5C_6)_2P^-$ group cause a P–W bond elongation of about 4 pm and a narrower W-P-W angle of 118° compared to 127° in the first two examples.

In contrast to the high π-acceptor potential of the pyridyl rings, the protonated phosphanide $PPy_2(H)$ in **2** is able to bridge two unsupported organometallic moieties. The charge density in the two lone pairs is well suited to accommodate two unsupported $\{W(CO)_5\}$ residues. The extent to which this lone pair density is able to act as a full four-electron donor, however, remains open. Further work for clarifying this question is under progress.

Experimental Section

X-ray investigation of **1** and **2**: The data sets were collected from oil-coated shock-cooled crystals on a BRUKER SMART-APEX diffractometer with D8 goniometer (graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) equipped with a low-temperature device in ω-scan mode at 100(2) K (**1**) and 173(2) K (**2**).[34] The data were integrated with SAINT[35] and an empirical absorption correction was applied with SADABS.[36] The structures were solved by direct methods (SHELXS-97)[37] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[37] Crystal data for **1**: $C_{12}H_{14}AlN_2P$, $M = 244.20\ g\,mol^{-1}$, monoclinic, space group $P2_1/c$, $a = 10.5952(7)$, $b = 8.6205(6)$, $c = 14.1052(9)$ Å, $\beta = 104.8630(10)°$, $V = 1245.21(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.303\ Mg\,m^{-3}$, $\mu = 0.265\ mm^{-1}$, 122823 reflections measured, 15640 independent, $R1(I>2\sigma(I)) = 0.0285$, $wR2(I>2\sigma(I)) = 0.0996$. Multipole refinement of **1**: $R(F^2) = 0.0155$, $R_w(F^2) = 0.0258$, GoF = 2.3508. In the refinement, the methyl groups share the same multipole parameters. Atomic densities are expanded to the hexadecapolar level for P, N, C1/C6, and C11/C12, and the octapolar level for all other carbon atoms. A bond-directed dipole for the H atoms is used. Crystal data for **2**: $C_{20}H_9N_2O_{10}PW_2$, $M = 835.96\ g\,mol^{-1}$, triclinic, space group $P\bar{1}$, $a = 9.3660(14)$, $b = 10.7247(16)$, $c = 13.2079(20)$ Å, $\alpha = 79.317(3)$, $\beta = 87.413(3)$, $\gamma = 67.030(3)°$, $V = 1199.8(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.314\ Mg\,m^{-3}$, $\mu = 9.703\ mm^{-1}$, 20962 reflections measured, 4768 independent, $R1(I>2\sigma(I)) = 0.0280$, $wR2(I>2\sigma(I)) = 0.0619$. CCDC 6611063 (**1**) and CCDC 611064 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] B. Cornils, W. A. Herrmann, I. T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt, *Multiphase Homogeneous Catalysis*, Wiley-VCH, Weinheim, **2005**.

[2] The latest Cambridge Crystallographic Data Centre CSD version 5.30 of November 2008 shows 2381 entries of bridging R_2P^- diorganophosphanides to at least a dinuclear metallic array, of which 2217 are transition metal complexes.

[3] a) H. Werner, *Angew. Chem.* **2004**, *116*, 956 – 972; *Angew. Chem. Int. Ed.* **2004**, *43*, 938 – 954.

[4] a) A. Albinati, F. Lianza, M. Pasquali, M. Sommovigo, P. Leoni, P. S. Pregosin, H. Rüegger, *Inorg. Chem.* **1991**, *30*, 4690 – 4692; b) P. Leoni, M. Pasquali, M. Sommovigo, F. Laschi, P. Zanello, A. Albinati, F. Lianza, P. S. Pregosin, H. Rüegger, *Organometallics* **1993**, *12*, 1702 – 1713.

[5] a) P. H. M. Budzelaar, P. W. N. M. van Leeuwen, C. F. Roobeek, A. G. Orpen, *Organometallics* **1992**, *11*, 23 – 25; b) T. Murahashi, T. Otani, T. Okuno, H. Kurosawa, *Angew. Chem.* **2000**, *112*, 547 – 550; *Angew. Chem. Int. Ed.* **2000**, *39*, 537 – 540.

[6] a) A. L. Balch, B. J. Davis, M. M. Olmstead, *J. Am. Chem. Soc.* **1990**, *112*, 8592 – 8593; b) A. L. Balch, B. J. Davis, M. M. Olmstead, *Inorg. Chem.* **1993**, *32*, 3937 – 3942.

[7] a) M. Sauthier, B. Le Guennic, V. Deborde, L. Toupet, J.-F. Halet, R. Réau, *Angew. Chem.* **2001**, *113*, 234 – 237; *Angew. Chem. Int. Ed.* **2001**, *40*, 228 – 231; b) F. Leca, M. Sauthier, V. Deborde, L. Toupet, R. Réau, *Chem. Eur. J.* **2003**, *9*, 3785 – 3795.

[8] a) T. Pechmann, C. D. Brandt, H. Werner, *Angew. Chem.* **2000**, *112*, 4069 – 4072; *Angew. Chem. Int. Ed.* **2000**, *39*, 3909 – 3911; b) T. Pechmann, C. D. Brandt, H. Werner, *Chem. Eur. J.* **2004**, *10*, 728 – 736.

[9] A. Steiner, D. Stalke, *J. Chem. Soc. Chem. Commun.* **1993**, 444 – 446.

[10] F. Baier, Z. Fei, H. Gornitzka, A. Murso, S. Neufeld, M. Pfeiffer, I. Rüdenauer, A. Steiner, T. Stey, D. Stalke, *J. Organomet. Chem.* **2002**, *661*, 111 – 127.

[11] a) H. Gornitzka, D. Stalke, *Angew. Chem.* **1994**, *106*, 695 – 698; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 693 – 695; b) H. Gornitzka, D. Stalke, *Organometallics* **1994**, *13*, 4398 – 4405.

[12] H. Gornitzka, D. Stalke, *Eur. J. Inorg. Chem.* **1998**, 311 – 317.

[13] S. Wingerter, M. Pfeiffer, A. Murso, C. Lustig, T. Stey, V. Chandrasekhar, D. Stalke, *J. Am. Chem. Soc.* **2001**, *123*, 1381 – 1388.

[14] a) M. Pfeiffer, F. Baier, T. Stey, D. Leusser, D. Stalke, B. Engels, D. Moigno, W. Kiefer, *J. Mol. Model.* **2000**, *6*, 299 – 311; b) M. Pfeiffer, A. Murso, L. Mahalakshmi, D. Moigno, W. Kiefer, D. Stalke, *Eur. J. Inorg. Chem.* **2002**, 3222 – 3234.

[15] M. Pfeiffer, T. Stey, H. Jehle, B. Klüpfel, W. Malisch, V. Chandrasekhar, D. Stalke, *Chem. Commun.* **2001**, 337 – 338.

[16] Gas-phase calculations. All frequencies are positive. Topological analyses were performed with AIM2000 and integration of atomic basins with DGRID-4.2 and BASIN-4.2.

[17] N. K. Hansen, P. Coppens, *Acta Crystallogr. Sect. A* **1978**, *34*, 909 – 921.

[18] A. Volkov, P. Macchi, L. J. Farrugia, C. Gatti, P. R. Mallinson, T. Richter, T. Koritsanszky, XD2006—A Computer Program Package for Multipole Refinement, Topological Analysis of Charge Densities and Evaluation of Intermolecular Energies from Experimental and Theoretical Structure Factors, **2006**.

[19] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372 – 1377; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785 – 789; c) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297 – 3305; d) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165 – 169; e) M. Häser, R. Ahlrichs, *J. Comput. Chem.* **1989**, *10*, 104 – 111; f) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346 – 354; g) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119 – 124; h) M. von Arnim, R. Ahlrichs, *J. Chem. Phys.* **1999**, *111*, 9183 – 9190.

[20] F. Biegler-König, J. Schönbohm, D. Bayles, *J. Comput. Chem.* **2001**, *22*, 545 – 559.

[21] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, **1990**.

[22] J. Henn, D. Ilge, D. Leusser, D. Stalke, B. Engels, *J. Phys. Chem. A* **2004**, *108*, 9442 – 9452.

[23] N. Kocher, D. Leusser, A. Murso, D. Stalke, *Chem. Eur. J.* **2004**, *10*, 3622 – 3631.

[24] A. J. Ashe III, *Top. Curr. Chem.* **1982**, *105*, 125 – 155.

[25] J. F. Nixon, *Chem. Rev.* **1988**, *88*, 1327 – 1362.
[26] M. Kohout, DGrid/Basin, v 4.2, Radebeul, **2007**.
[27] a) P. R. Mallinson, T. Koritsanszky, E. Elkaim, N. Li, P. Coppens, *Acta Crystallogr. Sect. A* **1988**, *44*, 336 – 342; b) J. Schefer, D. Schwarzenbach, P. Fischer, T. Koetzle, F. K. Larsen, S. Haussühl, M. Rüdlinger, G. McIntyre, H. Birkedal, H.-B. Bürgi, *Acta Crystallogr. Sect. B* **1998**, *54*, 121 – 128; c) E. A. Zhurova, Y. Ivanov, V. Zavodnik, V. Tsirelson, *Acta Crystallogr. Sect. B* **2000**, *56*, 594 – 600; d) F. Haarmann, H. Jacobs, M. Reehuis, A. Loose, *Acta Crystallogr. Sect. B* **2000**, *56*, 988 – 992.
[28] a) K. Meindl, J. Henn, *Acta Crystallogr. Sect. A* **2008**, *64*, 404 – 418; b) K. Meindl, J. Henn, N. Kocher, D. Leusser, K. A. Zachariasse, G. M. Sheldrick, T. Koritsanszky, D. Stalke, *J. Phys. Chem. A* **2009**, *113*, 9684 – 9691.
[29] a) T. Stey, J. Henn, D. Stalke, *Chem. Commun.* **2007**, 413 – 415; b) T. Stey, M. Pfeiffer, J. Henn, S. K. Pandey, D. Stalke, *Chem. Eur. J.* **2007**, *13*, 3636 – 3642.
[30] U. Vogel, K.-C. Schwan, M. Scheer, *Eur. J. Inorg. Chem.* **2004**, 2062 – 2065.
[31] B. Hoge, C. Thösen, T. Herrmann, I. Pantenburg, *Inorg. Chem.* **2003**, *42*, 3633 – 3641.
[32] A. Steiner, D. Stalke, *Organometallics* **1995**, *14*, 2422 – 2429.
[33] a) G. Becker, H. P. Beck, *Z. Anorg. Allg. Chem.* **1977**, *430*, 77 – 90; b) G. Becker, W. Becker, M. Schmidt, W. Schwarz, M. Westerhausen, *Z. Anorg. Allg. Chem.* **1991**, *605*, 7 – 23; c) G. Becker, M. Schmidt, W. Schwarz, M. Westerhausen, *Z. Anorg. Allg. Chem.* **1992**, *608*, 33 – 42.
[34] a) D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171 – 178; b) T. Kottke, R. J. Lagow, D. Stalke, *J. Appl. Crystallogr.* **1996**, *29*, 465 – 468; c) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615 – 619.
[35] Bruker AXS Inc., SAINT, v 7.23 A, Madison (WI), USA, **2006**.
[36] G. M. Sheldrick, SADABS, v 2006/2, Göttingen, **2006**.
[37] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122.

