Tungsten Tris(pyrazolyl)borate Cage Expansion by Formal Insertion of an Alkylidyne Group into a Tungsten−Nitrogen Bond

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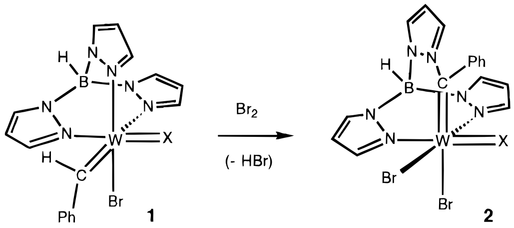
Alkylidyne ligands undergo coupling[1] with carbonyl,[2] isocyanide,[3] and thiocarbonyl[4] ligands. Furthermore, the formal coupling of two alkylidyne ligands has been demonstrated.[5] The ease of coupling appears to increase as the metal−ligand π orbitals of the coupling partners decrease in energy and approach the π level of the metal−carbon triple bond.[1,6] This trend prompted us to explore situations in which the metal−ligand orbitals of potential coupling partners are at lower energies than metal−carbon π bonds. This would be the case in alkylidyne imido and oxo metal systems.[7] In the known alkylidyne ligand coupling systems, the metal center features six metal−ligand π electrons. Since alkylidyne imido or oxo metal systems possess two additional electrons in the form of lone pairs located on the oxo or imido ligands, the establishment of the general alkylidyne ligand coupling condition would require a two-electron oxidation. In the search for systems stable enough to withstand such potentially harsh oxidizing conditions, we considered metal complexes containing tris(pyrazolyl)borate as an ancillary ligand ligand. Tris(pyrazolyl)borate metal cages have proven to be robust molecular anvils, supporting ligand transformations under very demanding conditions.[8−10] The tris(pyrazolyl)borate-substituted tungsten alkylidene oxo and imido complexes **1** were chosen as the starting point for this study.[11] The oxidative activation of these complexes could be preceded by deprotonation of the alkylidene ligand or might be followed by deprotonation. In either case, the metal−carbon multiple bond would be expected to participate in a bond-forming step. The execution of this scheme did not result in alkylidyne−imido or −oxo coupling, but rather led to the insertion of an alkylidyne group into the tungsten tris(pyrazolyl)borate cage. This transformation is not only the first formal insertion of an alkylidyne group into a metal−nitrogen single bond, but also represents the first case of a metal tris(pyrazolyl)borate cage expansion. The failure of the imido and oxo ligands to undergo coupling probably reflects the strength of the W−N and W−O multiple bonds.[12]



1 **2**

a: X = NCMe$_3$; **b**: X = N-1-adamantyl; **c**: X = NC$_6$H$_3$Me$_2$-2,6; **d**: X = O

Complexes **1** were prepared starting from tungsten hexacarbonyl via the bis(pyridine)-substituted tungsten alkylidyne complex [W(CPh)Br(CO)$_2$(py)$_2$].[13] After introduction of the tris(pyrazolyl)borate (Tp) ligand, the complex [W(CPh)(Tp)(CO)$_2$][14] was treated with bromine (THF, −78 °C to rt) to afford [W(CPh)(Tp)Br$_2$].[6c,15,16] Treatment of this complex with primary amines in CH$_2$Cl$_2$ or with water/silica in THF gave the imido complexes **1a−c** and the oxo complex **1d** as yellow solids in 55−98% yield.[11,17] Attempts to deprotonate the complexes **1** were not conclusive. Therefore, direct oxidation with bromine was investigated. Addition of bromine to a cold (−78 °C) solution of the oxo complex **1d** in CH$_2$Cl$_2$ caused an immediate disappearance of the brown-red color of bromine, followed by a darkening of the reaction solution upon warming to room temperature. The imido complexes **1a−c** behaved in a similar way. In the reactions of **1b,c**, NEt$_3$ was added before warming to room temperature (in order to neutralize liberated HBr). After removal of the solvent, the products **2a−d** were isolated by extraction and recrystallization.[18] The proton NMR spectra of complexes **2** show the presence of the CPh unit and the imido ligands for **2a−c**, but no resonances for the former benzylidene hydrogen atoms. ^{13}C NMR resonances in the range of δ 250−260 were assigned to the former benzylidene carbon atoms. This chemical shift range signals multiple bonding between the CPh

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(1) Mayr, A.; Bastos, C. M. *Prog. Inorg. Chem.* **1992**, *40*, 1.

(2) (a) Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, T. L.; Huttner, G. *Angew. Chem.* **1976**, *88*, 649; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 632. (b) Uedelhofen, W.; Eberl, K.; Kreissl, F. R. *Chem. Ber.* **1979**, *112*, 3376. (c) Fischer, E. O.; Friedrich, P. *Angew. Chem.* **1979**, *91*, 345; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 327. (d) Sheridan, J. B.; Pourreau, D. B.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 289. (e) Gamble, A. S.; Birdwhistell, K. R.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 1818. (f) James, A. P.; Stone, F. G. A. *J. Organomet. Chem.* **1986**, *310*, 47. (g) Protasiewicz, J. D.; Masschelein, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 808. (h) Mayr, A.; Bastos, C. M.; Chang, R. T.; Haberman, J. X.; Robinson, K. S.; Belle-Oudry, D. A. *Angew. Chem.* **1992**, *104*, 802; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 747.

(3) (a) Filippou, A. C.; Grünleitner, W. *Z. Naturforsch. B* **1989**, *44*, 1023. (b) Lippard, S. J.; Carnahan, E. M. *J. Chem. Soc., Dalton Trans.* **1991**, 699. (c) Bastos, C. M.; Daubenspeck, N.; Mayr, A. *Angew. Chem.* **1993**, *105*, 793; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 743. (d) Fraústo Da Silva, J. J. R.; Pellinghelli, M. A.; Pombeiro, A. J. L.; Richards, R. L.; Tiripicchio, A.; Wang, Y. *J. Organomet. Chem.* **1993**, *454*, C8.

(4) (a) Mayr, A.; Lee, T.-Y. *Angew. Chem.* **1993**, *105*, 1835; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1726. (b) Lee, T.-Y.; Mayr, A. *J. Am. Chem. Soc.* **1994**, *116*, 10300.

(5) (a) McDermott, G. A.; Mayr, A. *J. Am. Chem. Soc.* **1987**, *109*, 580. (b) Mayr, A.; Bastos, C. M.; Daubenspeck, N.; McDermott, G. A. *Chem. Ber.* **1992**, *125*, 1583.

(6) (a) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146. (b) Wilker, C. N.; Hoffmann, R.; Eisenstein, O. *Nouv. J. Chim.* **1983**, *7*, 535. (c) Filippou, A. C.; Hofmann, P.; Kiprof, P.; Schmidt, H. R.; Wagner, C. *J. Organomet. Chem.* **1993**, *459*, 233.

(7) Weinstock, I. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1991**, *113*, 135.

(8) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

(9) See, for example: (a) Deeming, A. J.; Donovan-Mtunzi, S. *Organometallics* **1985**, *4*, 693. (b) Doyle, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 194. (c) Beck, J.; Strähle, J. *Z. Naturforsch. B* **1987**, *42*, 255. (d) Roberts, S. A.; Young, C. G.; Kipke, C. A.; Cleland, W. E., Jr.; Yamanouchi, K.; Carducci, M.; Enemark, J. H. *Inorg. Chem.* **1990**, *29*, 3650. (e) Egan, J. W.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1990**, *112*, 2445. (f) Kitajima, N.; Fujisawa, K.; Moro-oka, Y. *Inorg. Chem.* **1990**, *29*, 357.

(10) For oxidative modifications of peripheral sites on coordinated tris(pyrazolyl)borate ligands, see: Reinaud, O. M.; Theopold, K. H. *J. Am. Chem. Soc.* **1994**, *116*, 6979.

(11) (a) Blosch, L. L.; Abboud, K.; Boncella, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7066. (b) Gamble, A. S.; Boncella, J. M. *Organometallics* **1993**, *12*, 2814.

(12) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*, Wiley: New York, 1988.

(13) (a) Fischer, E. O.; Ruhs, A.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 805. (b) McDermott, G. A.; Dorries, A. M.; Mayr, A. *Organometallics* **1987**, *6*, 925.

(14) Davis, J. H.; Lukehart, C. M.; Sacksteder, L. A. *Organometallics* **1987**, *6*, 50.

(15) Jeffery, J. C.; McCleverty, J. A.; Mortimer, M. D.; Ward, M. D. *Polyhedron* **1994**, *13*, 353.

(16) [W(CPh)(Tp)Br$_2$]: Green crystals, 94%. ^{1}H NMR (CD$_2$Cl$_2$) δ 8.21 (3H, pz-H^3), 7.80 (2H, pz-H^5), 7.76 (1H, pz−H^5), 7.64 (m, 2H, Ph−H^{3,5}), 6.96 (d, 2H, Ph-H^{2,6}), 6.74 (t, 1H, Ph-H^4), 6.38 (m, 3H, pz-H^4); ^{13}C NMR (CD$_2$Cl$_2$) δ 329.8 (WC). Anal. Calcd for WC$_{16}$H$_{15}$Br$_2$N$_6$B: C, 29.75; H, 2.34; Br, 24.75. Found: C, 29.57; H, 2.43; Br, 24.55.

unit and tungsten, although the W−C coupling constant of 163 Hz for **2b** indicates that the interaction is not as strong as in a typical metal−carbon triple bond. The spectroscopic data thus suggest that the CPh fragment is connected to another group, i.e. has participated in a bond-forming step.

The solid state structure[19] of **2b** (see Figure 1) revealed that the net result of the reaction was the insertion of the CPh group into one of the W−N bonds of the tungsten tris(pyrazolyl)borate cage. The strained nature of the tris(pyrazolyl)borate-substituted alkylidene ligand gives rise to some unusual geometric features. On the basis of electronic considerations, the preferred orientation of the alkylidene ligand would be parallel to the axis of the metal−nitrogen bond.[20] However, because the pyrazolyl group is firmly anchored to the boron atom, this orientation cannot be attained. The dihedral angle N(1)−W−C(20)−C(21) of 15.3(6)° may serve as a measure for the enforced misalignment of the alkylidene ligand. The pyrazolyl group is also prevented from connecting to the alkylidene carbon atom in a regular trigonal fashion. The W−C(20)−N(7) angle is 135°, 15° larger than normal.[21] Interestingly, this distortion is not accompanied by any adjustment of the W−C(20)−C(21) angle (120°). The N(7)−C(20)−C(21) angle is squeezed to a mere 104°. This is in marked contrast to the distortions of alkylidene ligands induced by agostic interactions.[22] In those cases, the C−R group of a CHR ligand "follows" the C−H group, leaving the H−C−R angle at about 120°.

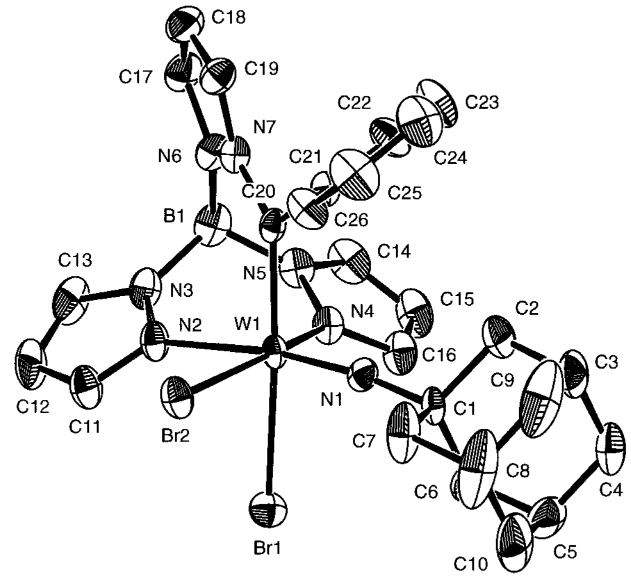

Figure 1. Molecular structure of **2b**. Selected bond distances (Å) and bond angles (deg): W−Br(1) 2.713(1), W−Br(2) 2.539(2), W−C(20) 2.067(8), W−N(1) 1.700(7), W−N(2) 2.266(6), W−N(4) 2.094(6), C(1)−N(1) 1.455(9), C(20)−C(21) 1.48(1), C(20)−N(7) 1.450(9); Br(1)−W−C(20) 170.1(2), Br(1)−W−N(1) 82.5(2), Br(2)−W−C(20) 98.4(2), Br(2)−W−N(1) 95.7(2), Br(2)−W−N(4) 164.1(2), C(20)−W−N(1) 98.0(3), C(20)−W−N(2) 90.0(3), C(20)−W−N(4) 88.0(3), N(1)−W−N(2) 171.9(3), N(1)−W−N(4) 97.8(3), W−C(20)−C(21) 120.3(5), W−C(20)−N(7) 135.2(5), W−N(1)−C(1) 172.1(6), C(21)−C(20)−N(7) 104.2(6).

In conclusion, attempts to achieve alkylidyne−imido or −oxo coupling resulted in the formal insertion of an alkylidyne group into one of the W−N single bonds of a tungsten tris(pyrazolyl)borate cage. It can be expected that similar insertion reactions of alkylidyne ligands will occur with other σ-bonded ligands.[23] This work also shows that tris(pyrazolyl)borate ligands may not be quite as innocent as is generally assumed. Under the proper conditions, especially in high oxidation state systems, the pyrazolyl−metal bonds appear to be able to participate easily in chemical transformations.

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Supporting Information Available: Data collection and refinement details and listings of atomic coordinates, thermal parameters, bond lengths, and bond angles of complex **6b** (8 pages). See any current masthead page for ordering and Internet access instructions.

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(17) **1a**: ^{1}H NMR (CD_2Cl_2) δ 10.46 (s, CHPh, 1H), 8.18, 8.06, 8.02 (d, 1H each, pz-H^3), 7.74, 7.72, 7.62 (d, 1H each, pz-H^5), 7.36 (m, 2H, Ph-$H^{3,5}$), 7.21 (d, 2H, Ph-$H^{2,6}$), 6.98 (t, 1H, Ph-H^4), 6.35, 6.29, 6.17 (m, 1H each, pz-H^4), 4.5−3.5 (br, 1H, BH), 1.57 (s, $C(CH_3)_3$, 9H). Anal. Calcd for $WC_{20}H_{25}BrN_7B$: C, 37.65; H, 3.95; Br, 12.52. Found: C, 37.43; H, 4.05; Br, 12.39. **1b**: ^{1}H NMR ($CDCl_3$) δ 10.39 (s, 1H, CPh), 8.20−6.97 (pz, Ph), 4.5−3.5 (br, 1H, BH), 2.14 (s, 3H, adamantyl), 2.11 (s, 6H, adamantyl), 1.63 (s, 6H, adamantyl); ^{13}C NMR ($CDCl_3$) δ 287.2 (CHPh). Anal. Calcd for $C_{26}H_{31}BBrN_7W$: 43.61; H, 4.61; H, 4.63; Br, 11.16. Found: C, 43.46; H, 4.17; Br, 11.0. **1c**: ^{1}H NMR (CD_2Cl_2) δ 11.33 (s, 1H, CHPh), 8.63−6.16 (pz, Ph, $C_6\mathit{H}_2Me_3$), 4.5−3.5 (br, 1H, BH), 2.37 (s, 3H, *p*-CH_3), 2.01 (s, 6H, *o*-CH_3); ^{13}C NMR (CD_2Cl_2) δ 281.3 (J_{WC} = 143.7 Hz, CHPh). Anal. Calcd for $C_{25}H_{27}BBrN_7W$: C, 42.89; H, 3.89; Br, 11.41. Found: C, 42.63; H, 4.06; Br, 11.17. **1d**: ^{1}H NMR (CD_2Cl_2) δ 11.04 (s, 1H, CHPh), 8.36, 8.35 (d, 1H each, pz-H^3), 7.86 (d, 2H, pz-$H^{3,5}$), 7.80, 7.72 (d, 1H each, pz-H^5), 7.60 (m, 2H, Ph-$H^{3,5}$), 7.49 (d, 2H, Ph-$H^{2,6}$), 6.97 (m, 1H, Ph-H^4), 6.42, 6.32, 6.28 (m, 1H each, pz-H^4); ^{13}C NMR (CD_2Cl_2) δ 294.0 (J_{WC} = 150.5 Hz, CHPh). Anal. Calcd for $WC_{16}H_{16}BrON_6B$: C, 32.97; H, 2.77; Br, 13.71. Found: C, 32.99; H, 2.93; Br, 13.61.

(18) **2a**: Extraction and recrystallization with ether, yellow crystals, 18%. ^{1}H NMR ($CDCl_3$) δ 8.81, 8.07, 7.92 (d, 1H each, pz-H^3), 7.86, 7.62, 6.70 (d, 1H each, pz-H^5), 6.45, 6.39, 6.38 (m, 1H each, pz-H^4), 7.35 (m, 2H, Ph-H-3,5), 7.14 (m, 3H, Ph-$H^{2,4,6}$), 4.5−3.5 (br, 1H, BH), 1.16 (s, 9H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 252.5 (WC). Anal. Calcd for $WC_{20}H_{24}Br_2N_7B$: C, 33.51; H, 3.37; Br, 22.29. Found: C, 33.60; H, 3.27; Br, 23.54. **2b**: Extraction and recrystallization with ether, yellow crystals, 64%. ^{1}H NMR (CD_2Cl_2) δ 8.57, 7.98, 7.87 (d, 1H each, pz-H^3), 7.80, 7.59, 6.60 (d, 1H each, pz-H^5), 6.37, 6.30, 6.18 (m, 1H each, pz-H^4), 7.26 (m, 2H, Ph-$H^{3,5}$), 7.04 (m, 3H, Ph-$H^{2,4,6}$), 5.0−4.0 (br, 1H, BH), 1.88 (m, 9H, adamantyl), 1.40 (s, 6H, adamantyl); ^{13}C NMR (CD_2Cl_2) δ 253.5 (J_{WC} = 162.8, WC). **2c**: THF solution, extraction and recrystallization with CH_2Cl_2, yellow crystals, low isolated yield. ^{1}H NMR (CD_2Cl_2) δ 8.68, 8.03, 7.99, 7.64, 7.06, 7.03, 6.88, 6.86, 6.83, 6.81, 6.80, 6.53, 6.35, 6.24 (pz, Ph, C_6H_2), 5.0−4.0 (br, 1H, BH), 3.10, 2.30, 1.11 (3H each, CH_3); ^{13}C NMR (CD_2Cl_2, 300 MHz) δ 259.5 (WC). Anal. Calcd for $WC_{25}H_{26}Br_2N_7B$: C, 38.55; H, 3.36; Br, 20.51. Found: C, 38.44; H, 3.18; Br, 20.38. **2d**: Extraction and recrystallization with ether/acetone, red crystals, 35%. ^{1}H NMR (acetone-d_6) δ 8.45, 8.35, 8.31 (d, 1H each, pz-H^3), 8.24, 7.86, 7.31 (d, 1H each, pz-H^5), 6.82, 6.64, 6.26 (m, 1H each, pz-H^4), 7.41 (m, 2H, Ph-$H^{3,5}$), 7.06 (m, 3H, Ph-$H^{2,4,6}$), 4.5−3.5 (br, 1H, BH). Anal. Calcd for $WC_{16}H_{15}Br_2ON_6B$: C, 29.04; H, 2.59; Br, 24.15. Found: C, 30.46; H, 3.00; Br, 23.91.

(19) Crystals of the composition **2b**·CH_3CN were grown from acetonitrile. The acetonitrile of crystallization is not shown in Figure 1. $C_{26}H_{30}N_7BBr_2W\cdot CH_3CN$, FW = 836.09, $P_{1(bar)}$, a = 13.077(7) Å, b = 13.342(4) Å, c = 10.221(6) Å, α = 112.45(2)°, β = 108.77(3)°, γ = 84.72(3)°, V = 1881.0(4) Å^3, Z = 2, μ(Mo Kα) = 63 500 cm^{-1}, 5924 unique reflections, $0° < 2\theta < 56°$, R = 0.048, R_w = 0.056. All intensity measurements were made at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and a variable-rate, $\omega-2\theta$ scan technique. Empirical absorption corrections were applied. The structures were solved by conventional heavy-atom methods and refined by full-matrix least squares. All calculations were performed using the TEXRAY programs.

(20) Schofield, M. H.; Schrock, R. R.; Park, L. Y. *Organometallics* **1991**, *10*, 1844.

(21) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983.

(22) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667.

(23) For the insertion of an alkylidyne group into a metal−aryl bond, see: Abbenhuis, H. C. L.; Feiken, N.; Haarman, H. F.; Grove, D. M.; Horn, E.; Spek, A. L.; Pfeffer, M.; van Koten, G. *Organometallics* **1993**, *12*, 2227.