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Intramolecular thioacyl hydroboration: synthesis of $[W(\eta^2\text{-}S_2CR)(CO)_2\{\eta^3\text{-}HB(pz)_2(SCH_2R)\}]$ (pz = pyrazol-1-yl, R = $C_6H_4Me\text{-}4$)

Anthony F. Hill *,† **and John M. Malget**

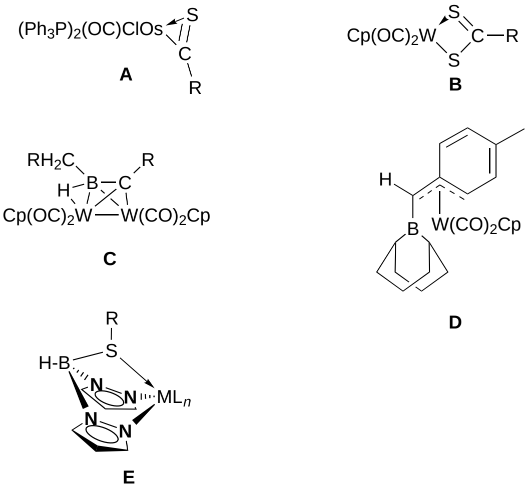
Department of Chemistry, Imperial College of Science, Technology and Medicine,
South Kensington, London SW7 2AY, UK

The sequential treatment of $[W(\equiv CR)Br(CO)_4]$ (R = C_6H_4-Me-4) with sulfur and $K[H_nB(pz)_{4-n}]$ (n = 1 or 2; pz = pyrazol-1-yl) provided $[W(\eta^2\text{-}S_2CR)(CO)_2\{HB(pz)_3\}]$ or $[W(\eta^2\text{-}S_2CR)(CO)_2\{\eta^3\text{-}HB(pz)_2(SCH_2R)\}]$, the latter *via* an unusual reduction of the alkylidyne–tungsten linkage.

The addition of elemental sulfur to alkylidyne complexes provides either thioacyl (**A**, Scheme 1, Group 8 metals)[1] or dithiocarboxylate (**B**, Group 6 metals)[2] complexes depending on the metal centre involved (Scheme 1). Within Group 6, only dithiocarboxylate complexes have been isolated, with no evidence, to date, for the intermediacy of thioacyls, however plausible these might be. The hydroboration of metal–carbon triple bonds has been demonstrated using external boranes,[3] and the results obtained (**C**, **D**) reflect the analogy with carbon–carbon multiple bonds. Furthermore, the interaction of alkylidyne ligands with carbaborane co-ligands is itself a field enjoying intense study,[4] although in many cases, it is clear that the intramolecular hydroboration processes often follow initial proton-induced alkylidene formation. Herein we report the unexpected combination of these two aspects of alkylidyne chemistry, *viz*. the sulfur-induced coupling of alkylidyne and dihydrobis(pyrazolyl)borate ligands to provide a co-ordinated bis(pyrazolyl)thiolatoborate (**E**).

The reaction of $[W(\equiv CR)Br(CO)_4]$ (hereafter R = C_6H_4-Me-4)‡ with elemental sulfur at low temperature provides a thermolabile complex which, although not yet isolated, is assumed to be either '$[W(\eta^2\text{-}S_2CR)Br(CO)_4]$' **1a** or '$[W(\eta^2\text{-}SCR)Br(CO)_4]$' **1b**. This assumption is supported by (*i*) the analogy with the compound $[W(\eta^2\text{-}S_2CR)(CO)_2(\eta\text{-}C_5H_5)]$ which results from the reaction of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with sulfur[2] and (*ii*) the formation of the thermally stable dithiocarboxylate complex $[W(\eta^2\text{-}S_2CR)(CO)_2\{HB(pz)_3\}]$§ **2** (pz = pyrazol-1-yl) on treatment with $K[HB(pz)_3]$ (Scheme 2).

Two processes are plausible. (*i*) The formation of a thioacyl species (**1b**) which reacts slowly with $K[HB(pz)_3]$ to provide $[W(\eta^2\text{-}SCR)(CO)_2\{HB(pz)_3\}]$ and then rapidly with the excess sulfur present to provide **2**. (*ii*) Alternatively, the dithiocarboxylate (**1b**) may be formed directly, and then react with $K[HB(pz)_3]$ to provide **2**. Unfortunately, attempts to isolate either **1a** or **1b** by varying conditions or reagent stoichiometry have so far met with failure. This intermediacy of the thioacyl species (**1b**) is, however, supported by the unusual results obtained from treating $[W(\equiv CR)Br(CO)_4]$ sequentially with sulfur and $K[H_2B(pz)_2]$: rather than the anticipated complex $[W(\eta^2\text{-}S_2CR)(CO)_3\{H_2B(pz)_2\}]$,¶ a deep purple complex was isolated which is formulated as the bis(pyrazolyl)thiolatoborate complex $[W(\eta^2\text{-}S_2CR)(CO)_2\{\eta^3\text{-}HB(pz)_2(SCH_2R)\}]$ **3** on the basis of spectroscopic data.§ Fast atom bombardment (FAB) mass spectral data confirm the gross formulation: in addition to a clear molecular ion, fragmentations are observed due to sequential decarbonylation. In contrast to a structured infrared absorbance, typical of the '$H_2B(pz)_2$' ligand, a single sharp ν(BH) stretch is observed at 2507 cm^{-1}. Both the intensity profile and position of the carbonyl absorbances for **3** are very similar to those for **2**. The ^1H NMR data indicate two chemically distinct pyrazolyl and tolyl environments in addition to an AB system arising from the diastereotopic methylene group of the SCH_2R substituent. Finally, the $^{13}C\text{-}\{^1H\}$ NMR spectrum reveals



Scheme 1 Cp = $\eta^5\text{-}C_5H_5$, R = $C_6H_4Me\text{-}4$

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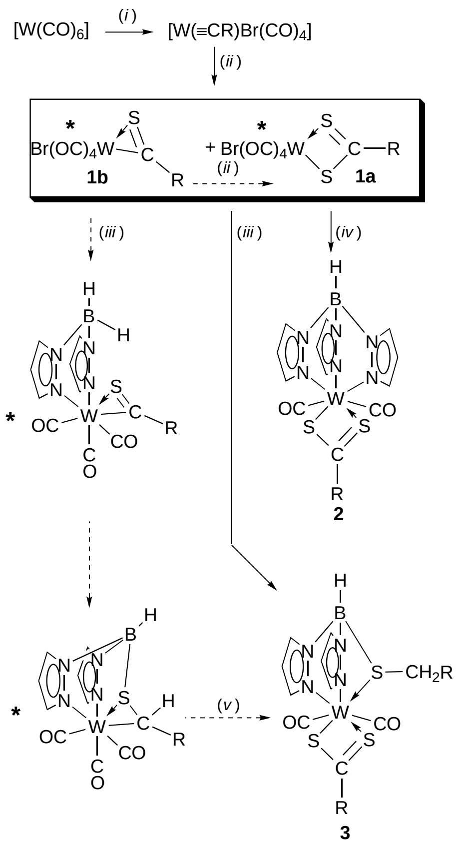
† E-Mail: a.hill@ic.ac.uk

‡ Prepared *in situ* from the successive treatment of $[W(CO)_6]$ with $LiR{\cdot}LiBr$ and $(CF_3CO)_2O$.

§ Data for **2**: $[W(\equiv CR)Br(CO)_4]$ (0.50 g)‡ and sulfur (0.05 g) in thf (50 cm^3) were stirred for 10 h at −10 °C. $K[HB(pz)_3]$ (0.21 g) was added and the mixture stirred for 12 h. The solvent was removed, the residue chromatographed (silica gel, hexane–diethyl ether, 5:1) and the purple eluate crystallised from pentane (−78 °C). Yield 0.47 g (90%). IR (Nujol)/cm^{-1}: 2496 [ν(BH)], 1925, 1835 [ν(CO)]. NMR ($CDCl_3$, 25 °C): ^1H, δ 2.38 [s, 3 H, CH_3], 6.24 [t, 3 H, H^4 (pz), J(HH) = 2], 7.19, 7.77 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 7.22, 8.26 [d × 2, 6 H, $H^{3,5}$ (pz), J(HH) 2 Hz]; $^{13}C\text{-}\{^1H\}$, δ 243.9 [WCO], 215.8 [S_2C], 146.4–106.6 [C_6H_4 and pz], 21.6 [CH_3] (Found: C, 36.2; H, 2.8; N, 12.5. $C_{19}H_{17}BN_6O_2S_2W{\cdot}0.25\,CH_2Cl_2$ requires C, 36.1; H, 2.8; N, 13.1%). **3**: Similar treatment of $[W(\equiv CR)Br(CO)_4]$ (0.50 g) as above, replacing $K[HB(pz)_3]$ with $K[H_2B(pz)_2]$ (0.16 g) provided **3**. Yield 0.08 g (28% based on R). IR (Nujol)/cm^{-1}: 2507 [ν(BH)], 1930, 1836 [ν(CO)]. NMR ($CDCl_3$, 25 °C): ^1H, δ 2.24, 2.28 [s × 2, 6 H, CH_3], 2.61, 3.39 [AB, 2 H, SCH_2, J(HH) 13], 6.08, 6.22 [t × 2, 2 H, H^4 (pz), J(HH) 2], 6.95, 7.02 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 7.11, 7.73 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 7.52, 7.73, 7.82, 8.07 [d × 4, 4 H, $H^{3,5}$ (pz), J(HH) 2 Hz]; $^{13}C\text{-}\{^1H\}$, δ 245.8 [WCO, J(WC) 124], 241.8 [WCO, J(WC) 127 Hz], 226.8 [S_2C], 145.3–107.3 [C_6H_4 and pz], 39.5 [SCH_2], 21.7, 21.2 [CH_3]. FAB mass spectrum (*m*-nitrobenzyl alcohol): m/z 690 (43, $[M]^+$), 664 (6, $[M-CO]^+$), 634 (41, $[M-2CO]^+$), 558 (82%, $[M-2CO-C_7H_7]^+$) (Found: C, 41.5; H, 3.4; N, 7.9. $C_{24}H_{23}BN_4O_2S_3W$ requires C, 41.8; H, 3.4; N, 8.1%).

¶ This complex has been reported to result from the reaction of $[W(\equiv CR)(CO)_3\{H_2B(pz)_2\}]$ with sulfur.[5]



Scheme 2 Tetrahydrofuran, −10 °C, R = C_6H_4Me-4. (*i*) LiR·LiBr, $(CF_3CO)_2O$; (*ii*) $\frac{1}{4}$ S_8; (*iii*) K[$H_2B(pz)_2$]; (*iv*) K[HB(pz)$_3$]; (*v*) RCS_2H.
* Indicates proposed intermediate, not isolated

signals for two carbonyl ligands [δ 245.8, *J*(WC) 124; 241.8, *J*(WC) 127 Hz], the dithiocarboxylate carbon [δ 226.8] and a singlet resonance [δ 39.5] showing no coupling to tungsten thereby indicating that it is remote from the tungsten co-ordination sphere.

The mechanism which we favour (Scheme 2) for the formation of **3** remains equivocal, however we note that Carmona *et al.*[6] have recently discussed the intramolecular hydroboration of an acyl ligand by a $H_2B(pz)_2$ co-ligand. Should a thioacyl complex [W(η^2-SCR)(CO)$_3${η^2-$H_2B(pz)_2$}] be formed it is therefore plausible that intramolecular hydroboration of the thioacyl ligand provides [W{η^2-SCH(R)BH(pz)$_2$}(CO)$_3$]. The reaction of this species with RCS_2H (formed by hydrolysis of **1a**) could then produce the final product **3**. Further support for the intermediacy of a thioacyl complex is provided by our very recent isolation of a range of such complexes based on tungsten and molybdenum.[7]

The co-ordination chemistry of one pre-formed mixed thiolate–pyrazolyl borate has been mentioned once before[8] when it was suggested that the complex [Cu(SR){η^3-HB(Me$_2$pz)$_2$(SR)}] could serve as a model for the tetrahedral 'CuS_2N_2' site in some copper proteins. In principle this otherwise neglected class of scorpionate ligand should show a rich co-ordination chemistry, a direction we are currently investigating.

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