Synthesis of N-Bonded Diazoalkane Complexes *via* the Reaction of the Trimethylsilyldiazomethane Anion with $M(CO)_5PPh_3$ (M = Cr; W): *X*-Ray Structure of $W(CO)_4(PPh_3)[N_2C(SiMe_3)_2]$

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Two new N-bonded diazoalkane complexes $M(CO)_4(PPh_3)[N_2C(SiMe_3)_2]$ (**3a**, M = Cr; **3b**, M = W) have been synthesized from the reaction of the trimethylsilyldiazomethane anion $Me_3SiCN_2^-$ with the parent compounds $M(CO)_5(PPh_3)$ (**2a**, M = Cr; **2b**, M = W) in the presence of Me_3SiCl.

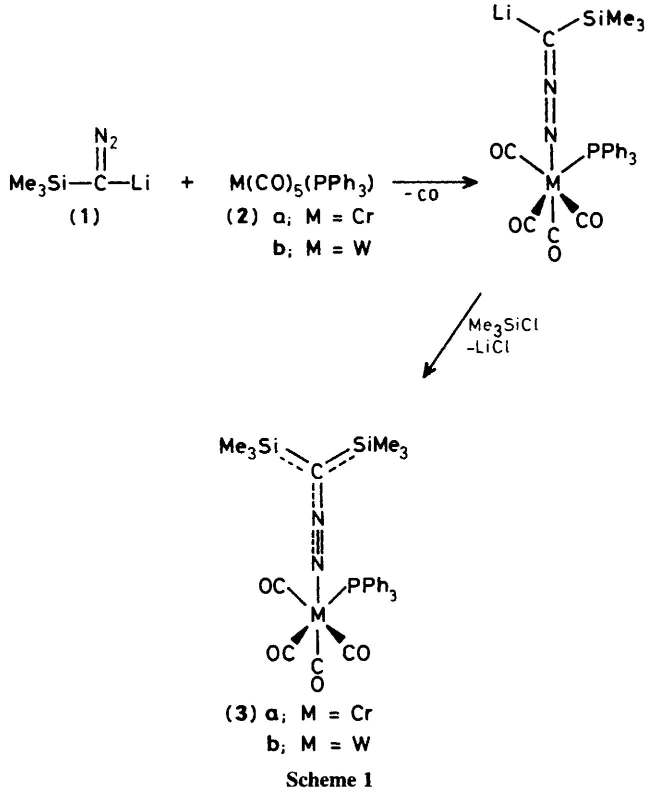
Diazoalkanes have proven to be exceedingly useful in organic chemistry mainly as precursors to carbenoid species.[1] Often a transition metal complex is employed to effect this transformation catalytically.[2] This explains the paucity of stable metal–diazoalkane complexes reported in the literature, despite (i) the many binding modes possible for a diazo moiety and (ii) the availability of cationic,[1] neutral,[1] and anionic[1,3] diazo ligands. For example, only a few complexes are known in which there is a terminal N-bonded diazo ligand (L_nM–N_2CR_2).[4—7] In these cases, linear, or simply or doubly bent metal–diazo entities have been proposed which emphasize the varying mode of attachment of these neutral ligands to transition metal systems and consequently their rich reactivity. In our attempts to prepare new diazo-substituted organometallic complexes with anionic diazo ligands,[8] we surprisingly discovered a novel route to N-bonded diazoalkane–metal complexes by displacement of a CO ligand.

The lithium salt of the trimethylsilyldiazomethane[3] (**1**) is easily prepared. We thought its addition to a metal–carbonyl complex such as $M(CO)_5(PPh_3)$ (**2a**, M = Cr; **2b**, M = W) would result in nucleophilic attack on the co-ordinated CO. The resulting anion could be quenched with Me_3SiCl to give new diazo-substituted Fischer-carbene complexes.[9] Alternatively, N_2 loss could occur, or be effected photolytically, to give metal–acetylene complexes.

To a tetrahydrofuran (THF) solution of (**2a**) or (**2b**) was added dropwise a THF solution of (**1**) (1.4 equiv.) at −78 °C. After slowly warming to −10 °C, Me_3SiCl (1.8 equiv.) was added. Upon removal of the solvent, extraction with pentane, and cooling (−25 °C), yellow crystals of (**3a**) (M = Cr, m.p. 106—108 °C) and (**3b**) (M = W, m.p. 104—105 °C) were obtained in 51 and 54% yield, respectively.

Spectroscopic properties† of the products were not in agreement with either of the expected products, but with a symmetrical structure such as (**3a,b**) (Scheme 1). However, because of the uncertainty in assigning the bonding mode of the diazo group, the structure of (**3b**) was confirmed by *X*-ray crystal structure analysis. The ORTEP view is illustrated in Figure 1 along with the atom numbering and the pertinent parameters.‡ The W^0 complex exhibits a distorted octahedral structure, with the diazo ligand co-ordinated through its terminal nitrogen atom *cis* to the phosphine group. The diazo ligand assumes a linear geometry [W–N(1)–N(2) 176.1(1)°, N(1)–N(2)–C(6) 170.(1)°]. Thus both N(1) and N(2) appear to possess approximate sp hybridization.

A striking feature of this complex is the unusually long W–N bond length [2.161(11) Å], which is significantly longer than comparable distances in other W–N–N species and signifies a single bond.[10] The distances N(1)–N(2) and N(2)–C(6) of



Scheme 1

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† (**3a**): ^1H n.m.r. ($CDCl_3$) δ 7.42 (m, PPh_3), 0.15 (s, $SiMe_3$); ^{31}P n.m.r. ($CDCl_3$) δ 58.9 p.p.m.; ^{13}C n.m.r. (CD_2Cl_2) δ 226.7 (d, J_{PC} 3.6 Hz), 223.4 (d, J_{PC} 12.9 Hz), 220.5 (d, J_{PC} 13.6 Hz), 137.3 (d, J_{PC} 31.7 Hz, C-*ipso*), 133.6 (d, J_{PC} 11.1 Hz, C-*ortho*), 129.9 (s, C-*para*), 128.7 (d, J_{PC} 9.0 Hz, C-*meta*), −0.19 (s, $SiMe_3$); C-*diazo* not observed; i.r. (pentane, cm^{-1}): 2012w, 1925m, 1907s (νCO); *m/z* 612 (M^+), 584 (M^+ −CO), 556 (M^+ −2CO), 314 (M^+ $-3CO-N_2C(SiMe_3)_2$].

(**3b**): ^1H n.m.r. ($CDCl_3$) δ 7.41 (m, PPh_3), 0.15 (s, $SiMe_3$); ^{31}P n.m.r. ($CDCl_3$) δ 22.9 p.p.m.; ^{13}C n.m.r. (CD_2Cl_2) δ 204.5 (d, J_{PC} 27.8 Hz), 204.1 (d, J_{PC} 6.0 Hz), 200.8 (d, J_{PC} 6.0 Hz), 136.6 (d, J_{PC} 36.7 Hz, C-*ipso*) 133.6 (d, J_{PC} 11.6 Hz, C-*ortho*); 129.9 (s, C-*para*), 128.4 (d, J_{PC} 9 Hz, C-*meta*), −0.51 (s, $SiMe_3$); i.r. (pentane, cm^{-1}): 2016w, 1923(m), 1906(brs) (νCO); *m/z* 744 (M^+), 716 (M^+ −CO), 688 (M^+−2CO), 660 (M^+−3CO), 446 [$M^+-3CO-N_2C(SiMe_3)_2$].

‡ *Crystal data:* (**3b**) $C_{29}H_{33}N_2O_4PSi_2W$, monoclinic, space group $P2_1/n$, $Z = 4$; $a = 13.084(2)$; $b = 17.012(3)$; $c = 14.981(3)$ Å; $\beta = 92.33(2)°$; $U = 3332(2)$ Å^3; $\mu(Mo\text{-}K_\alpha) = 34.46\ cm^{-1}$; $R = 0.0476$ ($R_w = 0.0533$) for 3840 reflections [$I > 3\sigma(I)$] measured on an Enraf-Nonius CAD-4 diffractometer. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

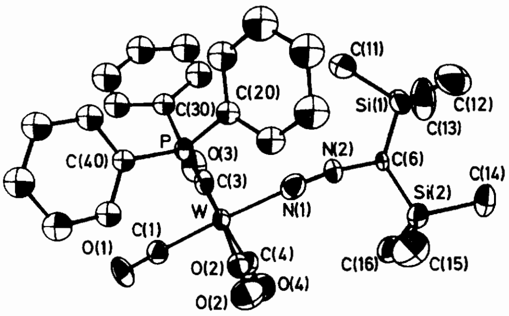

Figure 1. ORTEP drawing of W(CO)$_4$(PPh$_3$)[N$_2$C(SiMe$_3$)$_2$]. Main bond distances (Å): W–N(1) 2.161(11); W–P 2.528(3); W–C(1) 2.000(12); W–C(2) 2.060(14); W–C(3) 2.057(12); W–C(4) 1.924(4); N(1)–N(2) 1.165(15); N(2)–C(6) 1.34(1); C(6)–Si(1) 1.75(1); C(6)–Si(2) 1.77(1). Main bond angles(°): W–N(1)–N(2) 176(1); N(1)–N(2)–C(6) 170(1); N(2)–C(6)–Si(1) 116.5(7); N(2)–C(6)–Si(2) 110.8(7); Si(1)–C(6)–Si(2) 132.6(5); C(1)–W–N(1) 176.7(5).

1.165(15) and 1.34(1) Å are intermediate between double and triple, and single and double bonds respectively.[11] Similarly the C(6)–Si distance of 1.77(1) Å is shorter than a single C–Si bond (1.88 Å, av.).[8] This molecule could thus be described as a dinitrogen entity bridged by the W and C atoms, the SiMe$_3$ substituent acting as an electron acceptor stabilizing the complex by delocalisation of electrons from the N–N bond. This is one of the first structural examples of linear co-ordination of a diazoalkane to a metal complex.[12]

Our results show that activation of a diazoalkane, in this case by lithiation, giving rise to anionic diazo species, allows for its facile co-ordination to a metal even when a very labile ligand is not present. Note that in a separate experiment, trimethylsilyldiazomethane was added to a THF solution of (**2a**) or (**2b**) and no reaction was observed at 20 °C. The *X*-ray analysis of (**3b**) provides information on the binding of diazoalkanes to metal complexes. The application of these results to the synthesis and reactivity of new metal–diazo species is under current investigation.

Received, 1st June 1988; Com. 8/02166J

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