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Transition-Metal Complexes Featuring a Diazo Group on a Ligand: X-ray Crystal Structure of [*exo*-(Me_3SiCN_2)-η^5-C_6H_6]Mn$(CO)_3$

Régis Réau, Robert W. Reed, Françoise Dahan, and Guy Bertrand*

Laboratoire de Chimie de Coordination du CNRS,
205, route de Narbonne, 31077 Toulouse Cêdex, France

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Summary: [Bis(diisopropylamino)thioxophosphoranyl]- and (trimethylsilyl)diazomethane lithium salts react with $[(C_6H_6)Mn(CO)_3]^+PF_6^-$*, leading to [exo-*$(RCN_2)$*-*$\eta^5$*-*$C_6H_5$*]*$Mn(CO)_3$ *(4, R = (i-*$Pr_2N)_2P(S)$*; 5, R =* Me_3Si*), the first complexes with a diazo-functionalized ligand.*

Diazo derivatives react with a wide variety of transition metals.[1] In most cases, subsequent loss of nitrogen occurs, giving back the starting metal complex and a free carbene (catalytic process)[2] or alternatively affording carbene type complexes (stoichiometric process).[1,3] However, transition-metal complexes bearing the CN_2 group coordinated to the metal via the terminal nitrogen atom,[1,4] the π-system of the N═N bond,[1] or, more infrequently, the carbon atom[3b,c,5] have been reported.

Within the scope of our ongoing interests in developing diazomethane derivatives as useful synthetic building blocks,[6] it was tempting to prepare organometallic complexes bearing a diazomethane-functionalized ligand. To avoid the coordination of the diazo group, the metal center should possess no ancillary ligand[1,4b] and stand apart from the CN_2 moiety. It is known that nucleophiles attack the ring of cationic tricarbonyl(arene)manganese complexes by the face opposite to the metal,[7] and therefore we anticipated that by using diazo lithium salts as reagents, diazo-substituted cyclohexadienylmanganese complexes could be obtained.

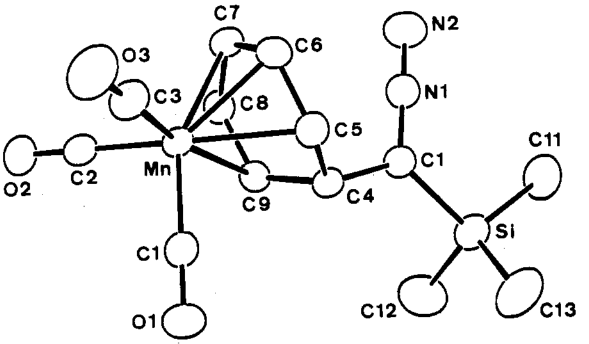

Figure 1. ORTEP drawing of **5**. Bond lengths (Å): Mn–C(1) = 1.798(2), Mn–C(2) = 1.799(2), Mn–C(3) = 1.796(2), C(4)–C(5) = 1.506(2), C(5)–C(6) = 1.388(3), C(6)–C(7) = 1.413(3), C(7)–C(8) = 1.412(3), C(8)–C(9) = 1.382(3), C(9)–C(4) = 1.508(3), C(10)–C(4) = 1.527(3), C(10)–Si = 1.856(2), C(10)–N(1) = 1.295(3), N(1)–N(2) = 1.136(3). Bond angles (deg): C(4)–C(10)–N(1) = 115.2(2), C(4)–C(10)–Si = 125.0(1), Si–C(10)–N(1) = 119.6(1), C(10)–N(1)–N(2) = 178.6(2). Dihedral angle (deg): C(6)–C(5)–C(9)–C(4) = 36.8(1).

Addition of a THF solution of the lithium salt of [bis(diisopropylamino)thioxophosphoranyl]diazomethane[8] or (trimethylsilyl)diazomethane[9] (**1** or **2**) to a heterogeneous THF solution of tricarbonyl(benzene)manganese hexafluorophosphate (**3**), at −78 °C readily gave a homogeneous orange solution. After warming to 0 °C, filtration, and removal of the solvent, complexes **4** and **5** were obtained as yellow-orange powders.

Compound **4** could not be isolated in analytically pure form. However, the features of the ^{13}C and ^1H NMR spectra,[10] and the values of phosphorus–C(4) and –C(5,9) (14.3 and 2.8 Hz, respectively) and phosphorus–H(4) (6.5 Hz) coupling constants, provided evidence for a cyclohexadienyl ligand substituted by a β-phosphorus atom.

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(10) **4**: ^1H NMR ($CDCl_3$) δ 1.21 (d, J_{HH} = 6.8 Hz, CH_3), 1.31 (d, J_{HH} = 6.8 Hz, CH_3), 3.4–4.0 (m), 4.92 (t-like, J_{HH} = 6.1 Hz, 2 H, $H^{6,8}$), 5.61 (t-like, J_{HH} = 5.3 Hz, 1 H, H^7); ^{13}C NMR ($CDCl_3$) δ 23.39 (s, CH_3), 23.65 (s, CH_3), 34.04 (d, J_{PC} = 14.3 Hz, C^4), 47.39 (d, J_{PC} = 5.1 Hz, NCH), 57.16 (d, J_{PC} = 2.8 Hz, $C^{5,9}$), 79.51 (s, C^7), 95.63 (s, $C^{6,8}$), 222.38 (s, CO) (the CN_2 carbon was not observed); ^{31}P NMR ($CDCl_3$) δ +63.4 ($^3J_{PH^4}$ = 6.5 Hz, $^3J_{PH(i\text{-}Pr)}$ = 17.2 Hz); FT-IR ($CDCl_3$, ν (cm^{-1})) 2044 (CN_2), 2022, 1935 (CO). **5**: mp 93–94 °C; ^1H NMR ($CDCl_3$) δ 0.13 (s, 9 H, $SiCH_3$), 2.52 (t, J_{HH} = 5.8 Hz, 1 H, H^4), 2.79 (t-like, J_{HH} = 6.1 Hz, 2 H, $H^{5,9}$), 4.24 (t-like, J_{HH} = 5.3 Hz, 2 H, $H^{6,8}$), 4.92 (t-like, J_{HH} = 5.3 Hz, 1 H, H^7); ^{13}C NMR ($CDCl_3$) δ −1.60 (s, $SiCH_3$), 31.73 (s, C^4), 45.99 (s, CN_2), 57.54 (s, $C^{5,9}$), 79.24 (s, C^7), 95.29 (s, $C^{6,8}$), 222.71 (s, CO); FT-IR ($CDCl_3$, ν (cm^{-1})) 2023, 1935 (CO); MS (m/z) 274 (M^+ − 2 CO).

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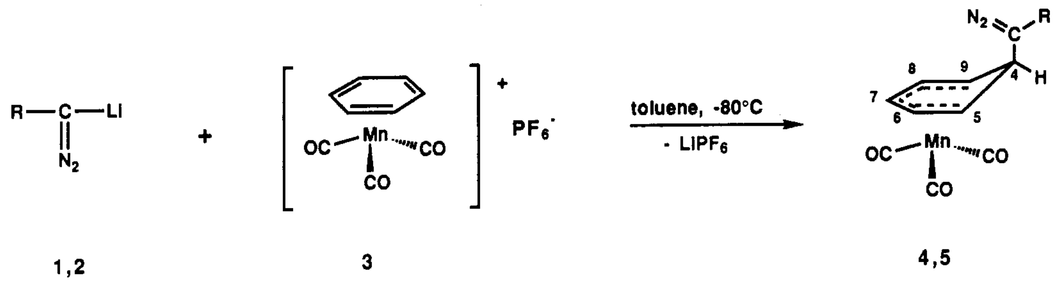
Scheme I



1,4 : R = (i-Pr$_2$N)$_2$P(S)

2,5 : R = Me$_3$Si

Moreover, in the IR spectrum, in addition to the characteristic CO absorptions of a (η^5-cyclopentadienyl)Mn(CO)$_3$ fragment, a strong band at 2044 cm^{-1} indicated the presence of a noncoordinated diazo group.[11]

Complex 5 crystallized from a cold toluene solution (75% yield, mp 93–94 °C). Its ^{1}H and ^{13}C NMR data[10] were in agreement with the proposed structure; of particular interest, a singlet was found at 45.9 ppm, in the range expected for a diazo carbon.[12] However, the diazo absorption, probably hidden by the strong CO bands (2023, 1935 cm^{-1}), was not observed by IR spectroscopy. Note that the diazo band of complex 4 shifts to lower wavenumber ($\Delta\nu$(CN$_2$) = 56 cm^{-1}) compared to [bis(diisopropylamino)thioxophosphoranyl]diazomethane, and thus a corresponding shift of the diazo band of (trimethylsilyl)diazomethane from 2048 cm^{-1} into the carbonyl region can be anticipated for 5. The structure of 5 and in particular the presence of the diazo moiety has been confirmed by an X-ray crystal structure analysis.[13] The ORTEP view is illustrated in Figure 1 along with the atom numbering scheme and the pertinent metric parameters.

The coordination sphere around the manganese atom is essentially that of a piano stool. The manganese atom is located 1.687(3) Å below the planar dienyl system (maximum deviation 0.008(2) Å). The cyclohexadienyl ring is folded at C(5)–C(9) with a dihedral angle of 36.8(1)°, and the (trimethylsilyl)diazo substituent is positioned exo, with the bulky trimethylsilyl group anti to the ring. The diazo moiety of complex 5 features geometric parameters similar to those of, for example, phenyl(trimethylsilyl)diazomethane (6).[14] In both compounds, the diazo atoms (C(10), N(1), N(2)) are almost linear (5, 178.6(2)°; 6, 178.8(1.4)°) and the N(1)–N(2) (5, 1.136(3) Å; 6, 1.130(16) Å) and C(10)–N(1) (5, 1.295(3) Å; 6, 1.280(17) Å) bond lengths are comparable: the diazo moiety of 5 is not disturbed by the metal center.

The presence of a transition-metal center, a reactive carbon–heteroatom bond, and as can be seen in Figure 1, an easily accessible diazo group, makes this new class of compounds a potentially powerful building block in organic and inorganic chemistry.

Supplementary Material Available: Tables giving crystal data and conditions and parameters for the data collection and refinement, atomic coordinates and isotropic thermal parameters for all atoms, anisotropic thermal parameters for the non-hydrogen atoms, bond distances and angles, and least-squares planes and deviations therefrom for compound 5 (7 pages). Ordering information is given on any current masthead page.

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(11) Coordination of the diazo group typically results in ν(CN$_2$) < 2000 cm^{-1}.[1-5]

(12) Horchler von Locquenghien, K.; Réau, R.; Bertrand, G. *J. Chem. Soc., Chem. Commun.* **1991**, 1192.

(13) Crystal data for compound 5: C$_{13}$H$_{15}$N$_2$O$_3$SiMn, fw 330.3, triclinic, space group $P\bar{1}$, a = 8.852(1) Å, b = 12.497(2) Å, c = 7.315(1) Å, α = 95.17(1)°, β = 90.47(1)°, γ = 102.06(1)°, V = 787.8(3) Å^3, Z = 2, d_{calc} = 1.392 g/cm^3, μ(Mo Kα) = 8.85 cm^{-1}. Data reflections were collected by a CAD4 Enraf-Nonius diffractometer in the 2θ range 3–25°. The structure was solved by direct methods and refined to R = 0.022 with 2381 reflections having $F_o{}^2 > 3\sigma(F_o)^2$, 185 variables, and S = 1.01.

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