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THE SYNTHESIS AND PROPERTIES OF BIS(μ-PHENYLDIAZENIDO)OCTACARBONYLDIMANGANESE

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Summary

Phenyldiazenidotrimethylsilane underwent reaction with bromopentacarbonylmanganese to give bis(μ-phenyldiazenido)octacarbonylmanganese. Triphenylphosphine caused fission of the phenyldiazenido bridge to form two mononuclear five coordinate complexes [$Mn(CO)_3N_2Ph(PPh_3)$] and [$Mn(CO)_2N_2Ph(PPh_3)_2$].

Introduction

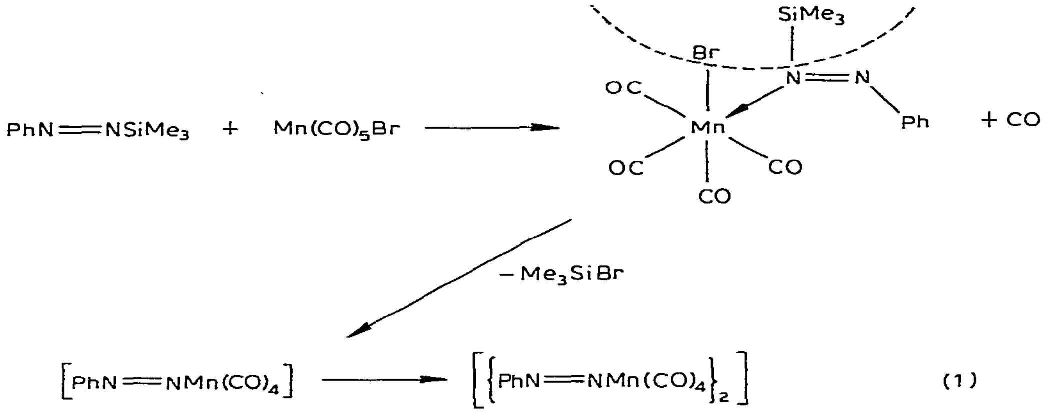
A number of organodiazenido complexes of metals have been reported in recent years [1,2] especially with their interest as models for the enzymatic reduction of dinitrogen [3]; and definitive structures for many of these have been reported [4]. The terminal ligands are known with both linear and bent M—N—N systems, but prior to the preliminary communication [5] of this work there had been no characterization of the aryldiazenido ligand in a μ_2 bridging mode.

The favoured reagents for the formation of transition metal aryldiazenido complexes have been the aryldiazonium salts, usually $ArN_2^+ BF_4^-$; but it is interesting to note in the context of this paper that reaction between $ArN_2^+ BF_4^-$ and $Na^+ [Mn(CO)_5]^-$ failed to yield an aryldiazenidocarbonyl of manganese [1a].

The use of nitrogen containing organosilanes has been a fruitful route to novel organonitrogen transition metal complexes [6], and access to a high yield synthesis [7] of the stable bright blue liquid aryldiazenidotrimethylsilanes [8] $ArN{=}NSiMe_3$, has encouraged us to investigate their potential as a useful source of the aryldiazenido ligand for transition metal complexes.

Results and discussion

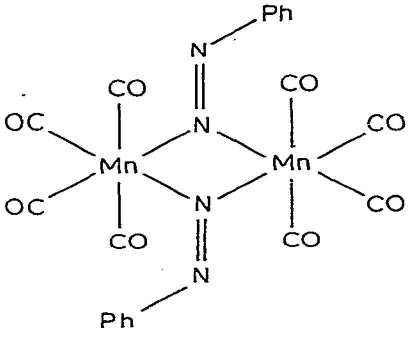
Bromopentacarbonylmanganese and phenyldiazenidotrimethylsilane underwent reaction at room temperature over a period of days to form bis(μ-phenyldiazenido)octacarbonyldimanganese. A proposed course for this reaction is outlined in eq. 1, where the first step involves displacement of carbon monoxide, followed by elimination of bromotrimethylsilane and subsequent dimerization.



(1)

We were unable to detect, or prepare, the proposed monomer intermediate, and the low yield of product suggests that other reactions may be taking place. However, the only other carbonyl containing product isolable in the work-up was decarbonyldimanganese.

The structure [9] of the dimeric bis(μ-phenyldiazenido)octacarbonyldimanganese is illustrated in I, where the phenyldiazenido group behaves as a formally three electron donor bridging group, analogous to X = Br[10], SMe[11], PPh_2[12] etc., in the $Mn_2(CO)_8X_2$ series of complexes



(I)

The infrared spectrum in the CO stretching region {2072(6.6), 2013(10), 2009(7.7) and 1976(8.6) cm^{-1}} is particularly characteristic of this class of complex [10c]. Whilst no molecular ion $[\{Mn(CO)_4N_2Ph\}_2]^+$ was observable in the mass spectrum, peaks corresponding to loss from two to eight carbonyl groups were observed. In addition to these dimeric ions which terminated with $[(MnN{=}NPh)_2]^+$, the monomeric ions $[Mn(CO)_4N{=}NPh]^+$, $[Mn(CO)_3N{=}NPh]^+$, $[Mn(CO)_2N{=}NPh]^+$ were recorded.

Despite the presence of the $[Mn(CO)_4N{=}NPh]^+$ ion in the mass spectrum we were unable to prepare any isolable mononuclear species [Mn(CO)$_n$N=NPh] from the action of high pressure carbon monoxide upon the dimer or indeed by any other method. This is in contrast to the dimeric manganese carbonyl halides [{Mn(CO)$_4$X}$_2$] (X = Cl, Br, I), which are converted to the monomeric Mn(CO)$_5$X species by carbon monoxide [10a].

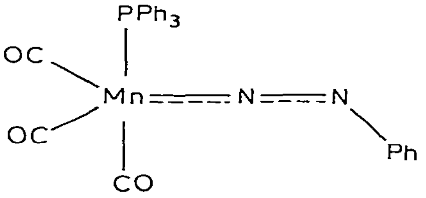
Treatment of [{Mn(CO)$_4$N=NPh}$_2$] with pyridine does not bring about bridge fission, and prolonged treatment causes complete decomposition. Triphenylphosphine does, however, undergo reaction according to eq. 2

$$[\{Mn(CO)_4N{=}NPh\}_2] + 2n\,Ph_3P \rightarrow 2[Mn(CO)_{4-n}N{=}NPh(Ph_3P)_n] + 2n\,CO \qquad (2)$$

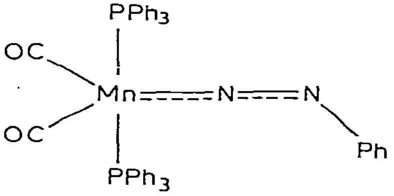
(n = 1, 2)

The mono- and bis-phosphine products are easily separated and characterised. In the phosphine bridge fission reactions of the corresponding dimeric manganese carbonyl halides the mononuclear products retain an octahedral coordination about manganese, and the halide ligands revert from formally three electron donors to one electron donors [10a]. In the phosphine fission of bis(μ-phenyldiazenido)octacarbonyldimanganese, the manganese changes from six to five coordinate and the aryldiazenido ligand retains its formally three electron donor role, albeit now terminal rather than bridging.

The proposed structures of the two phosphine derivatives are illustrated below (II and III).



(II)



(III)

They are exactly analogous to the previously reported nitrosyls [Mn(CO)$_3$(NO)(PPh$_3$)] [13] and [Mn(CO)$_2$(NO)(PPh$_3$)$_2$] [14], and also the isoelectronic cation [Fe(CO)$_2$N=NPh(PPh$_3$)]$^+$, the trigonal bipyramidal structure of which has been indicated by X-ray analysis [15].

The metal carbonyl stretching modes of [Mn(CO)$_3$N=NPh(PPh$_3$)] and [Mn(CO)$_2$N=NPh(PPh$_3$)$_2$] were ca. 10 cm^{-1} lower than the corresponding bands in the analogous nitrosyls [16] confirming the observation that the aryldiazenido appears to be a somewhat poorer π-acceptor than NO.

In the manganese system there are two other notable differences between the nitrosyl and phenyldiazenido ligands, thus although Mn(CO)$_4$NO can be isolated, the corresponding mononuclear manganese aryldiazenido carbonyl appears to be only capable of existance as phosphine substituted derivatives. Further, in contrast to [Mn(CO)$_4$N=NPh$_2$], [Mn(CO)$_4$)NO] dimerizes to [Mn$_2$(CO)$_7$(NO)$_2$] which contains a metal—metal bond, and is analogous to Fe$_2$(CO)$_9$ [16].

Experimental

All reactions were carried out routinely under an atmosphere of dry nitrogen, and solvent toluene was freshly distilled off potassium benzophenone. $Mn(CO)_5Br$[10] and $PhN{=}NSiMe_3$[7] were prepared by literature methods.

Interaction of bromopentacarbonylmanganese and phenyldiazenidotrimethylsilane

A solution of phenyldiazenidotrimethylsilane (3.65 g, 22.5 mmol) and bromopentacarbonylmanganese (4.75 g, 17.3 mmol) in toluene (50 ml) was stirred for 6 days at 26°C. Solvent was removed at 20°C/0.1 mmHg and decarbonyldimanganese (0.37 g) was sublimed from the residue (30°C/0.1 mmHg). Recrystallization of the remaining solid from toluene gave bis(μ-phenyldiazenido)-octacarbonyldimanganese (1.01 g, 19.5%) as yellow crystals, m.p. 134—136°C (dec.). Anal.: Found: C, 44.2; H, 1.92; N, 10.3. $C_{20}H_{10}N_4O_8Mn_2$ calcd.: C, 44.2; H, 1.84; N, 10.3%. Molecular weight 560 (vapour pressure osmometer in benzene), calculated 544.

Interaction of bis(μ-phenyldiazenido)octacarbonyldimanganese and triphenylphosphine

A solution of bis(μ-phenyldiazenido)octacarbonyldimanganese (0.055 g, 0.101 mmol) and triphenylphosphine (0.11 g, 0.42 mmol) in toluene (5 ml) was stirred for 3 days at 25°C and then chromatographed on a 30 × 2 cm alumina column. Elution with hexane/toluene (50/50) gave extraction of phenyldiazenidotricarbonyltriphenylphosphinemanganese, purified by recrystallization to give red crystals (0.012 g), m.p. 123—125°C. Anal.: Found, C, 64.3; H, 4.07; N, 5.60. $C_{26}H_{20}N_2O_2PMn$ calcd.: C, 64.1; H, 3.95; N, 5.53%. ν(CO) 2022 (10), 1957 (8) and 1919 (7) cm^{-1}, mass spectrum (three highest m/e) 506 $[M]^+$, 450 $[M - 2\ CO]^+$ and 422 $[M - 3\ CO]^+$. Further elution with hexane/ether (50/50) yielded phenyldiazenidodicarbonylbis(triphenylphosphine)manganese, purified by recrystallization to give red crystals (0.051 g), m.p. 163—165°C (dec.). Anal.: Found: C, 71.3, H, 4.89; N, 3.61. $C_{44}H_{35}N_2O_2P_2Mn$ calcd.: C, 71.4; H, 4.73; N, 3.78%. ν(CO) 1940 (7) and 1866 (10), mass spectrum (three highest m/e) 684 $[M - 2\ CO]^+$, 656 $[M - 2\ CO - N_2]^+$, 317 $[MnPPh_3]^+$.

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