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Novel Route to Cationic Nitrosyl Complexes. Displacement of Carbon Disulphide Coordinated to Iron

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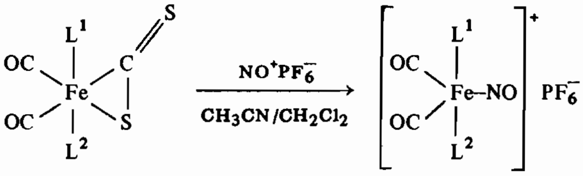
There is widespread interest [1] in the chemistry of transition metal nitrosyl complexes and some examples of their use as catalysts have also been reported [2]. Although a variety of routes leading to the coordination of the nitrosyl group by substitution reactions are known [1, 3] none of them has utilised carbon disulphide complexes as precursors.

It has already been shown (a) that carbon disulphide iron complex *Ia* allows the introduction of identical or mixed phosphorus ligands in the apical position of iron leading to stable $Fe(CO)_2(CS_2)L^1L^2$ derivatives containing strong Iron–CS_2 bonds [4] and (b) that the nucleophilicity of the carbon disulphide moiety is markedly enhanced by coordination in complexes of type I [5]. We now wish to report initial studies on the displacement of the nucleophilic η^2-CS_2 ligand by electrophilic assistance and that the nitrosyl cation selectively leads to the substitution of the carbon disulphide in complexes I, whereas competitive displacement of carbonyl could have been expected [3].

Experimental

Derivatives I in dichloromethane were treated with one equimolar amount of $(NO)(PF_6)$ in acetonitrile at room temperature. After a few minutes of stirring, good yields (85–95%) of cationic nitrosyliron complexes II were obtained by addition of ether. Compounds II recrystallized from dichloromethane–pentane mixture gave satisfactory analyses [II (yield, m.p.): IIa (95%, 190 °C) [3a]; IIb (85%, 140–145 °C); IIc (86%, 172 °C); IId (90%, 165 °C]. Their main spectroscopic characteristics are displayed in Table I.



I II

L^1, L^2: a (PPh_3, PPh_3), b (PMe_3, PMe_3),
c (PMe_3, PPh_3), d (PMe_2Ph, PPh_3)

Discussion

Of special interest are the nmr data of complexes II (Table I). Methyl protons of *equivalent* phosphorus ligands in IIb give a doublet indicating that no virtual coupling occurs as in the *trans* precursor Ib [4]. This is consistent with a lowering of the $^2J_{PP}$ value when the coordinated CS_2 was replaced by the NO^+ ligand. Indeed unsymmetrically substituted cations IIc and IId allowed measurement of the $^2J_{PP}$ value which is much lower (30.8 Hz and 31.5 Hz, respectively) than in Ic (161 Hz [4]). This low ^2J value cannot be attributed to an averaging of the coupling constant for it does not change significantly when the temperature of a solution of IId is lowered from 300 K to 223 K (^2J = 31.5 ± 1 Hz). It is likely that the decreasing J value depends on the nature of the $(NO)^+$ ligand rather than on the modification of the *trans* position of the phosphorus ligands. For the ^{13}C nmr

TABLE I. Spectroscopic Data of Complexes II.

	IR (cm^{-1})[a]		NMR (δ ppm)[b]			
	ν(CO)	ν(NO)	^1H	$^2J_{P-H}$	^{31}P[c]	$^2J_{PP}$
IIa	2055(s), 2000(vs);	1800 vs				
IIb	2040(s), 1985(vs);	1780 vs	2.10(d);	11 Hz;	28.70(s)	
IIc	2045(s), 1995(vs);	1780 vs	8.0 (m) 2.25(d);	12.5 Hz;	57.6 (d) 31.6 (d)	30.8 Hz
IId	2060(s), 2005(vs);	1800 vs	7.70(m) 2.57(d);	11 Hz;	57.7 (d) 34.3 (d)	31.5 Hz

[a] Nujol mull. [b] In CD_3COCD_3 solution. [c] Shifts downfield (+) from external H_3PO_4.

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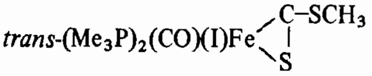
spectrum of IIc at 243 K which shows equivalent ^{13}CO [$\delta(CH_3CN) = 207.2$ ppm (q)] coupled with two different phosphorus nuclei ($^2J_{^{31}P-^{13}C} = 25$ Hz and 29 Hz) and the relative intensities of the carbonyl absorption bands [3a] are consistent with a trigonal bipyramidal rather than a square pyramidal geometry.

Similar compounds II containing identical phosphorus ligands and for which a trigonal bipyramidal geometry was suggested have already been prepared by B. F. G. Johnson and J. A. Segal [3a] by displacement of one carbonyl of $Fe(CO)_3(PR_3)_2$. However the present route offers several advantages: (a) carbon disulphide precursors I are much more stable than the corresponding $Fe(CO)_3L_2$ derivatives; this relative stabilisation is especially marked with phosphines possessing electron donating substituents and complexes Ib, Ic and Id are air stable even in solution; (b) attempts to introduced mixed ligands in the apical position of tricarbonyliron complexes were not successful or needed drastic conditions [6], whereas high yields of unsymmetrically substituted complexes I can be easily obtained [4]; (c) this novel reaction allows the transformation of a nucleophilic derivative I into a very electrophilic compound II.

Rather than by substitution at the metal the carbon disulphide displacement probably takes place by initial interaction of the nitrosyl cation with the nucleophilic uncoordinated sulfur atom which is known to react with other electrophilic reagents [5]. This process is consistent with the selectivity of the substitution for which no displacement of carbonyl occurs. Moreover, when the uncoordinated sulfur atom is bonded to an alkyl group as in the derivative  *trans*-$(Me_3P)_2(CO)(I)Fe(\eta^2\text{-}C(SCH_3)S)$ the addition of the nitrosyl cation does not lead to the removal of the sulfur containing ligand.

Syntheses of nitrosyl complexes containing functionalized phosphorus ligands by the route described here are currently under investigation.

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