Journal of

The Chemical Society,

Chemical Communications

NUMBER 13/1976 7 JULY

Transition Metal Complexes Containing the Bis(trifluoromethyl)nitroxy Ligand

By BRIAN L. BOOTH, ROBERT N. HASZELDINE,* and ROBERT G. G. HOLMES

(Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD)

Summary Stable Ir^{III} and Pt^{II} complexes containing the ligand $(CF_3)_2NO$ have been obtained by oxidative addition of the radical $(CF_3)_2NO\cdot$ to Ir^{I} and Pt^{0} compounds and by metathetical chlorine atom exchange using $Hg[ON(CF_3)_2]_2$; $(CF_3)_2NONa$ reacts with the cations $[M(CO)(MeCN)(PPh_3)_2]^+$ (M = Rh or Ir) to afford the Ir^{I} and Rh^{I} complexes $[M(CO)\{(CF_3)_2NO\}(PPh_3)_2]$, and with the Pt^{II} cations $[PtX(CO)L_2]^+$ (X = Cl, Br; L = PPh$_3$: X = Cl, L = AsPh$_3$) to give the compounds of type $[PtX\{CO{\cdot}ON(CF_3)_2\}L_2]$.

ALTHOUGH bis(trifluoromethyl)nitroxy derivatives of main group elements may often be prepared by reaction of the radical $(CF_3)_2NO\cdot$,[1] very little information is available about derivatives of the transition metals, apart from a report of an unstable cobalt(II) species, $[Co\{ON(CF_3)_2\}_2]$,[2] and a communication on the manganese(I) complex $[(CF_3)_2NOMn(CO)_5]$ formed by reaction of the radical with $[HMn(CO)_5]$.[3] In our hands this last reaction has always resulted in a mixture of the reported complex and $[Mn_2(CO)_{10}]$, and we have not yet succeeded in obtaining a pure sample. Thermally- and air-stable Ir^{I}, Ir^{III}, Rh^{I}, and Pt^{II} derivatives of the $(CF_3)_2NO$ ligand have now been prepared by the methods outlined in Scheme 1, doubtless applicable to the preparation of $(CF_3)_2NO$ derivatives of other transition metals.

Oxidative addition of $(CF_3)_2NO\cdot$ occurs readily at room temperature in benzene or carbon tetrachloride to give the complexes (I)—(III) as white, crystalline solids with ν(CO) bands typical of Ir^{III} complexes (see Table), and strong bands at 1260, 1150, and 950 cm^{-1} for ν(C–F); the $(CF_3)_2NO$ ligand also gives a singlet at *ca.* 10 p.p.m. to low field of CF_3CO_2H in the ^{19}F n.m.r. spectra ($CDCl_3$ solution). The ^1H n.m.r. spectrum of compound (III) shows an apparent triplet centred at τ 7·28 (apparent J_{P-H} 5·9 Hz), establishing that the two phosphine ligands remain *trans* in this compound, and presumably in the other compounds, although the stereochemistry of the remaining ligands cannot be unambiguously assigned. The white crystalline Pt^{II} complex (IV) has been fully characterised by i.r. and ^{19}F n.m.r.

Oxidative addition

$$[IrCl(CO)L_2] \xrightarrow{(CF_3)_2NO\cdot} [IrCl\{ON(CF_3)_2\}_2(CO)L_2]$$

(I) L = PPh$_3$; (II) L = AsPh$_3$;
(III) L = PPh$_2$Me

$$[Pt(PPh_3)_2(C_2H_4)] \xrightarrow{(CF_3)_2NO\cdot} [Pt(PPh_3)_2\{ON(CF_3)_2\}_2]$$

(IV)

Halogen displacement

$$[PtCl_2(AsPh_3)_2] \xrightarrow{[(CF_3)_2NO]_2Hg} [Pt\{ON(CF_3)_2\}_2(AsPh_3)_2]$$

(V)

$(CF_3)_2NONa$ reaction with metal carbonyl cations

$$[PtX(CO)L_2]^+BF_4^- \xrightarrow{(CF_3)_2NONa} [PtX\{CO{\cdot}ON(CF_3)_2\}L_2]$$

(VI) L = PPh$_3$, X = Cl
(VII) L = PPh$_3$, X = Br
(VIII) L = AsPh$_3$, X = Cl.

Ligand displacement

$$[M(CO)(MeCN)(PPh_3)_2]^+ClO_4^- \xrightarrow{(CF_3)_2NONa} [M\{ON(CF_3)_2\}(CO)(PPh_3)_2]$$

(IX) M = Ir; (X) M = Rh

SCHEME 1. Preparative methods for bis(trifluoromethyl) nitroxy compounds.

spectroscopy, but its stereochemistry has not yet been established. These examples of radical additions to low-valent iridium and platinum complexes substantiate recent observations[4] that a free-radical oxidative addition mechanism can occur readily, and can often be preferred to alternative mechanisms.

TABLE

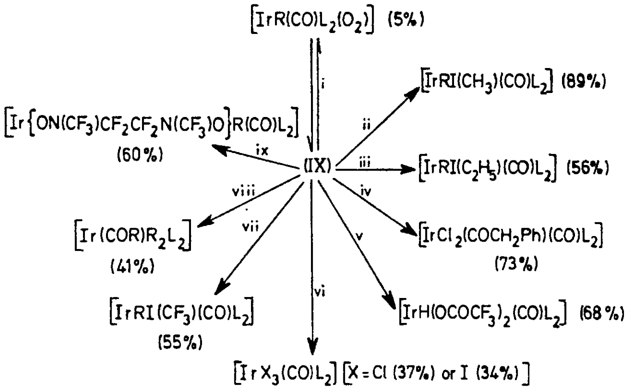
$(CF_3)_2NO$ derivatives of transition metals

Compound[a]	Yield/%	M.p. (decomp.) /°C	ν(M–CO) /cm^{-1}
(I)·CCl_4	50	170[b]	2052
(II)	44	150—5[b]	2058
(III)	49	140[b]	2058
(IV)	54	175—177[b]	
(V)	48	148—152[b]	
(VI)	47	196[c]	
(VII)·CH_2Cl_2 ..	66	180[c]	
(VIII)	36	142[c]	
(IX)·tetrahydrofuran	70	190—200[b]	1957
(X)·0·5CH_2Cl_2 ..	51	160—180[b]	1960

[a] Satisfactory analysis obtained; the crystals sometimes contained solvent of crystallisation. [b] Decomposition point before melting. [c] Decomposition on melting.

Use of the mercurial $[(CF_3)_2NO]_2Hg$ in $CFCl_3$ solutions in the metathetical halogen exchange readily yields the triphenylarsine compound (V), and although the similar reaction with $[PdCl_2(PPh_3)_2]$ results only in decomposition, preliminary investigations have shown that other Pt^{II} complexes and a Au^{I} complex can be prepared, suggesting that the method may have wider application for the synthesis of other $(CF_3)_2NO$ derivatives of transition metals. It is not known whether these reactions involve oxidative addition followed by reductive elimination of a mercury(II) halide, or a four-centre exchange reaction as suggested for main group halides.[5]

The sodium salt of bis(trifluoromethyl)hydroxylamine, $(CF_3)_2NONa$,[6] reacts only with the most reactive metal carbonyl cations, in which the CO ligand has a high electrophilic character,[7] to afford the novel derivatives (VI)—(VIII), characterised by the disappearance in the i.r. spectrum of the metal carbonyl stretching vibration and the appearance of a new carbonyl absorption in the region of 1707—1709 cm^{-1}; their ^{19}F n.m.r. spectra ($CDCl_3$ solution) show a singlet in the range 24·1—24·8 p.p.m. downfield from CF_3CO_2H for the $(CF_3)_2NO$ group, compared with 11·70 and 11·75 p.p.m. for the Pt^{II} derivatives (IV) and (V) respectively. The sodium salt does not cause halide ion displacement from compounds such as $[IrCl(CO)(PPh_3)_2]$ or $[RhCl(PPh_3)_3]$, or halogen-bridge cleavage reactions with, for example, $[\{PtCl(PPh_3)_2\}_2][BF_4]_2$, but it will displace weakly co-ordinated ligands from ionic rhodium and iridium complexes to give the complexes (IX) and (X).



$R = ON(CF_3)_2$, $L = PPh_3$

SCHEME 2. i, O_2, 1 atm; ii, MeI; iii, EtI; iv, $PhCH_2COCl$; v, CF_3CO_2H; vi, I_2 or Cl_2; vii, CF_3I; viii, $(CF_3)_2NO\cdot$; ix, $CF_3{\cdot}N(\dot{O})CF_2{\cdot}CF_2{\cdot}N(\dot{O}){\cdot}CF_3$.

The iridium complex (IX) undergoes oxidative addition reactions (Scheme 2); halogens or acyl halides result in replacement of the $(CF_3)_2NO$ ligand, whereas the reaction with an excess of $(CF_3)_2NO\cdot$ results in an interesting CO 'insertion' reaction which warrants further investigation.

We thank the S.R.C. for a research studentship (to R.G.G.H.).

(*Received, 3rd October* 1976; *Com.* 1133.)

---

[1] P. M. Spaziante, *M.T.P. Int. Rev. Sci., Inorg. Chem., Ser.* 1, 1972, **3**, 41; D. P. Babb and J. M. Shreeve, *Interscience Chem. Report*, 1971, 55; H. J. Emeléus, *Rec. Chem. Prog.*, 1971, **32**, 135.
[2] H. J. Emeléus, P. M. Spaziante, and S. M. Williamson, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3219.
[3] H. G. Ang, *Chem. Comm.*, 1968, 1320.
[4] A. Fusi, R. Ugo, F. Fox, A. Pasini, and S. Cenini, *J. Organometallic Chem.*, 1971, **26**, 417; J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osbourne, *J. Amer. Chem. Soc.*, 1972, **94**, 4043; M. F. Lappert and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 948.
[5] H. J. Emeléus, J. M. Shreeve, and P. M. Spaziante, *J. Chem. Soc.* (*A*), 1969, **431**; C. S. Wang and J. M. Shreeve, *Inorg. Chem.*, 1973, **12**, 81; H. J. Emeléus, P. M. Spaziante, and J. M. Shreeve, *Chem. Comm.*, 1968, 1251.
[6] R. E. Banks, R. N. Haszeldine, and D. L. Hyde, *Chem. Comm.*, 1967, 413.
[7] H. C. Clarke, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, 1969, **91**, 1346; R. J. Angelici, *Accounts Chem. Res.*, 1972, **5**, 335.