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Anisotropic Magnetic Shielding Effects on Co-ordinated Methyl Cyanide

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Although substituted metal halide complexes containing alkyl nitriles have been known for some years [1], these ligands have only recently been utilised more widely in preparative organometallic chemistry. They are readily replaced in the co-ordination sphere by other ligands and nitrile complexes have established themselves as excellent precursors for synthetic reactions [2–4]. We have recently demonstrated [5] that $[Mn(CO)_3(NCMe)_3]PF_6$ provides a convenient route to cationic manganese(I) carbonyl nitrile complexes and during this work we observed unusual chemical shifts for the nitrile proton resonances in the pmr spectra. These could be correlated with:

(i) The presence of ligands containing aryl groups (*e.g.* PMe_2Ph) in the co-ordination sphere, resulting in upfield shifts of variable magnitude; (ii) the presence of the tetraphenylborate anion which causes a large and regular upfield shift of ±0.7 ppm when compared with analogous hexafluorophosphate, perchlorate or tetrafluoroborate salts.

The aryl groups on co-ordinated phosphines have rarely been reported to exert an observable near neighbour anisotropic shielding effect on the protons of other ligands [6, 7]. Our results indicate that nitrile groups are particularly sensitive to this type of magnetic shielding, although the shifts are too irregular to be of use in identifying the methyl cyanide resonance in spectra that are complex. However, the above mentioned effect [2] will be shown to be sufficiently predictable to allow this shift to be used as a general means of identification of methyl cyanide resonances in a variety of complexes, particularly in cases where the resonances of other ligands are overlapping.

Experimental

All pmr spectra were recorded with Varian A-60A and HA-100 instruments. Complexes of iridium [8] and ruthenium [9] were prepared in this laboratory and will be fully described in forthcoming publications. Preparations of the hexafluorophosphate salts of the manganese(I) carbonyl cations have been described previously [5] for the ligands $P(OMe)_3$, PMe_2Ph and $P(OMe)_2Ph$. Isolation of the cations as the tetraphenylborate salts was carried out by an analogous procedure. The complex $[Mn(CO)_3(NCMe)(PMe_3)_2]PF_6$ has not been described previously and was prepared as pale yellow needles from $[MnBr(CO)_3(PMe_3)_2]$ and $AgPF_6$ in cold methyl cyanide solution [5] (Yield 78%. Found: C, 27.81; H, 4.16; N, 2.86. $C_{11}H_{21}F_6O_3N_1P_3Mn$ requires C, 27.69; H, 4.44; N, 2.93%. $\tau(CD_2Cl_2)$ 8.39 (d, PMe_3, J_{P-H} = 8.8Hz)). ν_{CO} (CH_2Cl_2) 2056w, 1967s, 1941m. M.P. 159–162 °C).

Results and Discussion

Unco-ordinated methyl cyanide exhibits a methyl singlet in the pmr spectrum at 8.05τ (CD_2Cl_2 solution). On co-ordination the ligand methyl resonance is normally shifted downfield, indicating decreased shielding at the methyl protons. This has been explained [10] in terms of an inductive effect within the molecule caused by donation of the nitrogen "lone pair" of electrons to the metal. This downfield shift is observed in $[Mn(CO)_3(NCMe)_3]PF_6$ and the hexafluorophosphate derivatives containing $P(OMe)_3$ and PMe_3 ligands (see Table I). The introduction of aryl ligands [$P(OMe)_2Ph$ and PMe_2Ph] results in a shift in the opposite direction, the magnitude of which is variable but generally dependent on the number of bonded phosphorus groups. The upfield shifts observed here are not restricted to manganese complexes but can explain abnormally high methyl cyanide resonances previously observed in certain iron and platinum compounds [11–13]. Comparison of the chemical shifts for the tetraphenylborate and hexafluorophosphate salts of the cations $[Mn(CO)_xL_y(NCMe)_z]^+$ [L = NCMe, PMe_3, PMe_2Ph, $P(OMe)_3$, $P(OMe)_2Ph$] demonstrates that the co-ordinated methyl cyanide resonance can be consistently shifted upfield by 0.5 ppm to 1.0 ppm due to the magnetic influence of the BPh_4^- anion. This can be explained by the positive end ($-CH_3$) of the methyl cyanide dipole being preferentially located above the plane of the benzene ring where the π electron density and also the diamagnetic shielding are greatest. The anomalous high resonance of free methyl cyanide in benzene solvent has been similarly explained [10]. The shifts provide a useful means of identifying the methyl cyanide resonances in these complexes, particularly in the case of the dimethylphenylphosphine derivatives where the resonance is obscured by that of the phosphine methyl protons.

TABLE II. Methyl Cyanide Resonances in Selected Complexes of Iridium [a] and Ruthenium.

Compound	Anion	Nitrile Methyl Resonance(τ)	Tolyl Methyl Resonance(τ)	Other Methyl Resonances(τ)
$[Ir\{P(OC_6H_3Me)_2(OC_6H_4Me)\}(NCMe)_3]X$	PF_6	7.28(1), 7.78(2)	7.48(1)(s), 7.72(2)(s)	
	BPh_4	8.21(1), 8.45(2)	7.54(1)(s), 7.74(2)(s)	
$[Ir\{P(OC_6H_3Me)_2(OC_6H_4Me)\}(NCMe)(PMe_2Ph)_2]X$	PF_6	7.62(1)	7.51(1)(s), 7.91(2)(s)	8.44(2)(d), J(P–H) = 9 8.62(2)(d), J(P–H) = 9
	BPh_4	8.66(1)	7.54(1)(s), 7.89(2)(s)	8.47(2)(d), J(P–H) = 8 8.8 (2)(d), J(P–H) = 8
$[Ir\{P(OC_6H_3Me)_2(OC_6H_4Me)\}(NCMe)(PMePh_2)_2]X$	PF_6	7.44(1)	7.63(1)(s) [b]	b
	BPh_4	8.39(1)	7.67(1)(s), 8.01(2)(s)	8.12(2)(d), J(P–H) = 8
$[Ru(cod)(NCMe)_4](X)_2$	PF_6 [c]	7.35(1), 7.59(1)		
$[Ru(cod)(4\text{-Me-py})_2(NCMe)_2](X)_2$	PF_6 [d]	7.32(1)		7.54(1)
	BPh_4 [e]	7.49(1)		7.59(1)

[a] Measured in CD_2Cl_2 solution, s = singlet, d = 1:1 doublet, figures in parentheses refer to relative peak intensities, J values reported in Hz. [b] Overlapping methyl phosphine and methyl tolyl resonances at τ = 7.94–8.02. [c] Measured in CD_3CN solution. [d] Measured in CD_3NO_2 solution. [e] $NaBPh_4$ (*ca.* 1 molar equivalent) added to CD_3NO_2 solution of $[Ru(cod)(4\text{-Me-py})_2(NCMe)_2][PF_6]_2$.

TABLE I. Methyl Cyanide Resonances in a Series of Cationic Manganese Complexes.

Compound	Anion(X)	Nitrile Resonance for Ligand (L), τ [a]				
			$P(OMe)_3$	PMe_3	$P(OMe)_2Ph$	PMe_2Ph
$[Mn(CO)_3(NCMe)_3]X$	PF_6	7.60(−0.45)				
	BPh_4	8.11 (+0.06)				
$[Mn(CO)_3L_2(NCMe)]X$	PF_6		7.64(−0.41)	7.67(−0.38)	8.47(+0.42)	b
	BPh_4		8.67 (+0.62)	8.65 (+0.60)	9.15(+1.10)	9.16(+1.11)
$[Mn(CO)_2L_2(NCMe)_2]X$	PF_6		7.64(−0.41)		8.24(+0.19)	b
	BPh_4		8.09 (+0.04)		8.87(+0.82)	8.88(+0.83)
$[Mn(CO)_2L_3(NCMe)]X$	PF_6		7.72(−0.33)		8.78(+0.73)	
	BPh_4		8.38 (+0.33)		9.43(+1.38)	

[a] Measured in CD_2Cl_2 solution. Figures in parentheses indicate shifts (ppm) from unco-ordinated methyl cyanide resonance, either downfield (−) or upfield (+). [b] Obscured by overlapping phosphine methyl resonance.

This effect is quite general for cationic compounds and has been used to analyse spectra of other, non-related methyl cyanide complexes synthesised in this laboratory. Thus the novel dimetallated iridium(III) complex [8] $[Ir\{P(OC_6H_3Me)_2(OC_6H_4Me)\}(NCMe)_3]PF_6$ exhibits four methyl resonances of ratio 1:1:2:2 (see Table II). The tris(*ortho*-tolyl)phosphite ligand gives rise to two methyl resonances in the ratio 1:2, due to one unmetallated and two *ortho*-metallated tolyl rings respectively, and the 1:2 ratio of the remaining two resonances can indicate either a facial or meridional methyl cyanide ligand arrangement. No phosphorus–nitrile coupling [5] was observed in this case. Isolation of the cation as the tetraphenylborate salt results in a shift of the resonances at τ7.28 and 7.78 to τ8.21 and 8.45 respectively, thus identifying these as the methyl cyanide resonances and allowing an unequivocal assignment of all four peaks in each spectrum. Pmr spectra of the phosphine substituted complexes $[Ir\{P(OC_6H_3Me)_2(OC_6H_4Me)\}L_2(NCMe)]PF_6$ (L = PMe_2Ph and $PMePh_2$) are complicated by additional methyl resonances, but the nitrile and phosphite peaks can be separated by the same procedure (see Table II).

The complex $[Ru(cod)(NCMe)_4](ClO_4)_2$ exhibits [14, 15] two methyl cyanide resonances of equal intensity at τ7.34 and 7.57. Studies [14] of analogous complexes using asymmetric dienes have resulted in the resonance at τ7.34 being assigned to the mutually *trans* methyl cyanide ligands. Reaction of $[Ru(cod)(NCMe)_4](PF_6)_2$ with 4-methyl-pyridine yields a product [9] $[Ru(cod)(4\text{-Me-py})_2(NCMe)_2](PF_6)_2$, exhibiting methyl resonances which are almost identical to those of the precursor (see Table II). Identification of the nitrile resonance in this case is not only of academic importance, but allows assignment of the stereochemistry of the product. On addition of sodium tetraphenylborate to the n.m.r. solution, only the resonance at τ7.32 is shifted upfield, indicating that the methyl cyanide ligands *trans* to the diene in $[Ru(cod)(NCMe)_4]^{2+}$ are most readily displaced by 4-methyl-pyridine in accordance with previous kinetic results [14].

Collectively, these observations demonstrate that the magnetic shielding effect of the tetraphenylborate anion can be generally used as a means of identifying methyl cyanide resonances in cationic transition metal compounds, regardless of the metal or the ligands involved. With methyl cyanide being increasingly widely used as a ligand, this additional technique for simplifying the spectra of its compounds should find wide application.

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