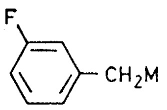
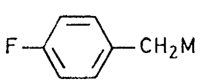
trans-Influence of Anionic, Neutral, and Bridging Ligands on the Nuclear Magnetic Resonance Spectra of Methyl- and Fluorobenzyl-bis(dimethylglyoximato)rhodium(III) Complexes. Some Observations on Bridge Formation

By **Claude Bied-Charreton** and **Alain Gaudemer**, Laboratoire de Chime de Coordination Bioorganique, Université Paris-Sud, 91405 Orsay, France
Carey A. Chapman, David Dodd, B. Dass Gupta, Michael D. Johnson,* and **Bill L. Lockman**, Department of Chemistry, University College, 20 Gordon St., London WC1H 0AJ
Bernard Septe, Institut de Chimie des Produits Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France

The ^{19}F and ^{1}H n.m.r. spectra of a series of 3- and 4-fluorobenzylbis(dimethylglyoximato)ligandrhodium(III) complexes have been recorded and compared with those of the corresponding cobalt(III) complexes. The chemical shifts of the fluorine substituents show that the strong electron-donating effects of the metallomethyl substituent is composed of a small hyperconjugative contribution which increases markedly in the order ligand = $I^- < [SCN]^- < Br^- \leqslant Cl^- \leqslant [N_3]^- < [NO_2]^- < [CN]^-$, and a very strong inductive contribution which increases slightly in the same order. The chemical shifts of the 4-fluorine substituents are paralleled by the ^{1}H chemical shifts of the benzylic methylene groups and of the methyl groups of the corresponding methylbis(dimethylglyoximato)ligandrhodium(III) complexes, and by the $^{13}C-^{1}H$ coupling of the methyl groups in the latter complexes. The ^{13}C chemical shifts show no correlation with any of the usual *trans*-effect parameters for a wide range of neutral and anionic *trans* ligands. Similar considerations have been applied to a number of bridged complexes in which fluorobenzyl- and/or other alkyl-bis(dimethylglyoximato)-rhodium(III) and -cobalt(III) complexes are bonded to the two ends of cyanide, azide, or thiocyanate ligands.

In previous papers we described the ^{19}F n.m.r. spectra [1-3] of some 3- and 4-fluorobenzyl metal complexes and demonstrated that several metallomethyl groups, such as $CH_2Mn(CO)_5$ [in (1) and (2)] and $CH_2Fe(CO)_2(\eta\text{-}C_5H_5)$ [in (3) and (4)] were, like many main-group metallomethyl groups, strong inductive electron-donating substituents which could also act as hyperconjugative electron-donating substituents toward the 4-fluorine substituent.[4,5] The groups $CH_2Co(Hdmg)_2L$, where Hdmg is the conjugate base of dimethylglyoxime and L is a unidentate ligand [in (5) and (6)] showed less-marked electron-donating character except where L was a strongly co-ordinating anionic ligand such as $[CN]^-$ or $[NO_2]^-$. The variations in the α-(methylene)-proton shifts of the bis(dimethylglyoximato)(fluorobenzyl)-cobalt(III) complexes (5) and (6) [2,3] were too small to detect any trends with the changing ligand L, to allow comparison with literature predictions,[6,7] or to show any correlation with fluorine chemical shifts. However, preliminary studies of the ^{1}H and ^{19}F n.m.r. spectra of similar organorhodium(III) complexes [*e.g.* (7) and (8)] suggested that the effect of axial ligand changes on both ^{19}F and ^{1}H chemical shifts were larger than in the corresponding organocobalt(III) complexes. Moreover, the presence of the magnetically active rhodium nucleus can provide additional information with which to test other approaches to *trans* effects using n.m.r. coupling constants.





	M		M
(1)	$Mn(CO)_5$	(2)	$Mn(CO)_5$
(3)	$Fe(CO)_2(\eta\text{-}C_5H_5)$	(4)	$Fe(CO)_2(\eta\text{-}C_5H_5)$
(5)	$Co(Hdmg)_2L$	(6)	$Co(Hdmg)_2L$
(7)	$Rh(Hdmg)_2L$	(8)	$Rh(Hdmg)_2L$

(9) $[Rh(^{13}CH_3)(Hdmg)_2L]$

In this paper are described studies of ^{19}F, ^{1}H, and ^{13}C n.m.r. spectra of a series of 3- and 4-fluorobenzylbis(dimethylglyoximato)rhodium(III) complexes and carbon-13-enriched bis(dimethylglyoximato)methylrhodium(III) complexes in which the *trans* axial ligand is anionic, neutral, or acts as a bridge to another metal centre.

RESULTS AND DISCUSSION

Preparation of Complexes.—As in previous work on the anionic cobaloxime * complexes, considerable difficulty was experienced in obtaining solid anionic organorhodoxime complexes free from the solvents used in their preparation and purification. In all the cases in which the individual complex salts were isolated, the analyses were satisfactory (Table 1) after allowance for solvent (CH_2Cl_2 or OEt_2) shown to be present in the solid by n.m.r. spectroscopy. However, since such complexes may dissociate in the solvents used for the spectral

---

* The terms cobaloxime and rhodoxime are trivial usage for bis(dioximato)-cobalt and -rhodium complexes.

[1] C. W. Fong and M. D. Johnson, *J.C.S. Perkin II*, 1973, 986.

[2] D. Dodd, M. D. Johnson, and C. W. Fong, *J.C.S. Dalton*, 1974, 58.

[3] D. Dodd and M. D. Johnson, *J.C.S. Dalton*, 1973, 1218.

[4] M. D. Johnson and N. Winterton, *J. Chem. Soc.* (*A*), 1970, 511.

[5] S. N. Anderson, D. H. Ballard, and M. D. Johnson, *Chem. Comm.*, 1971, 779.

[6] H. A. O. Hill and K. G. Morallee, *J. Chem. Soc.* (*A*), 1969, 554.

[7] W. C. Trogler, R. C. Stewart, L. A. Epps, and L. G. Marzilli, *Inorg. Chem.*, 1974, **13**, 1564.

measurements, it is more satisfactory to prepare them *in situ* from the corresponding purified, neutral, aquabis(dimethylglyoximato)organorhodium(III) complex [(7)—(9); L = OH_2] and a small excess (*ca.* 10% except where stated) of the relevant axial ligand L or axial ligand salt $[AsPh_4]L$. Since axial ligand exchange in these complexes is slow on the n.m.r. time scale, the presence of a sharp doublet * α-(benzyl or methyl)-proton resonance is indicative of the presence of a single complex in solution.

TABLE 1

Analytical data for organorhodoximes $[RhR(Hdmg)_2L]$ and $[AsPh_4][RhR(Hdmg)_2L]$

R	L	Entrained solvent [a]	Analysis (%) [b] C	H	N
$CH_2C_6H_4$-4	CN	$0.5CH_2Cl_2$	54.1	4.8	7.1
			(54.4)	(4.6)	(7.8)
	N_3		53.3	4.7	11.6
			(54.0)	(4.7)	(11.3)
	NCO	CH_2Cl_2,	51.9	4.6	6.6
		$0.25OEt_2$	(51.9)	(4.6)	(7.2)
	NO_2	$0.5CH_2Cl_2$,	51.5	4.6	8.2
		$0.25OEt_2$	(52.2)	(4.7)	(7.5)
	Cl	$0.5CH_2Cl_2$	51.8	4.6	6.7
			(52.5)	(4.6)	(6.2)
	Br	$0.5CH_2Cl_2$	49.3	4.4	5.9
			(50.0)	(4.4)	(5.9)
	OH_2		39.0	4.6	12.3
			(39.1)	(4.8)	(12.2)
$CH_2C_6H_4F$-3	OH_2		38.9	5.1	12.1
			(39.1)	(4.8)	(12.2)
Me	OH_2		29.0	4.7	14.7
			(29.5)	(5.2)	(15.3)

[a] Determined by n.m.r. in $CDCl_3$. [b] After allowance for entrained solvent and tetraphenylarsonium cation. Calculated values are given in parentheses.

TABLE 2

Fluorine-19 [a] and ^1H n.m.r. spectra of 3- and 4-fluorobenzylmetaloximes of the types (A) $[Z][M(CH_2C_6H_4F\text{-}x)(Hdmg)_2L]$, (B) $[M(CH_2C_6H_4F\text{-}x)(Hdmg)_2L]$, and (C) $[M(CH_2C_6H_4F\text{-}x)(Hdmg)(H_2dmg)L]$

			^{19}F, M = Rh					^1H, M = Rh	^{19}F, M = Co					Δδ (Rh − Co)
Type	L	Z	δ(4-F)	δ(3-F)	Δδ	$-\sigma_R^0$	$-\sigma_I$	$\delta(CH_2)$ [b]	δ(4-F) [c]	δ(3-F)	Δδ	$-\sigma_R^0$	$-\sigma_I$	(x = 4)
(A)	CN	$AsPh_4$	10.06	3.85	6.21	0.21	0.46	1.87 [d]	8.49	3.89	4.60	0.15	0.46	1.57
	NO_2	$AsPh_4$	8.88	3.63	5.25	0.18	0.43	1.91	7.80	3.68	4.12	0.14	0.44	1.08
	N_3	$AsPh_4$	8.58	3.49	5.09	0.17	0.40	1.93	7.60		(3.9) [e]	0.13		0.98
	NCO [f]	$AsPh_4$	8.60	3.58	5.01	0.17	0.42	2.12	7.50	3.64	3.86	0.13	0.43	1.10
	OCN [f]	$AsPh_4$	8.12		(4.6) [e]	0.15		2.32						
	Cl	$AsPh_4$	7.58	3.55	4.03	0.13	0.41	2.51	7.04	3.56	3.48	0.12	0.41	0.54
	Br	$AsPh_4$	7.52		(3.9) [e]	0.13		2.46	6.72		(3.2) [e]	0.11		0.80
	SCN [g]	$AsPh_4$	6.90		(3.4) [e]	0.12		2.77	6.78		(3.2) [e]	0.11		0.12
	I	$AsPh_4$	6.64	3.40	3.24	0.11	0.39	2.72	6.52	3.49	3.03	0.10	0.40	0.12
	I	PPr_4	6.62											
	I	NBu_4	6.74											
(B)	PPh_3		6.90	3.04	3.86	0.13	0.34		4.97	2.97	2.00	0.06	0.33	1.93
(C)	I [h]		4.59						2.90					
Other compounds														
MeC_6H_4F			5.58	1.20	4.38	0.14	0.08							
$[AsPh_4][O_2CCH_2C_6H_4F]$			5.92	1.85	4.07	0.13	0.18							
$FC_6H_4CH_2CO_2H$			2.36	0.10 [i]	2.26	0.07	−0.07							
$[Fe(CH_2C_6H_4F)(CO)_2(\eta\text{-}C_5H_5)]$			7.80	1.35	6.45	0.22	0.27							

[a] 10^{-4} mol complex in CH_2Cl_2 (0.5 cm^3); δ in p.p.m. relative to internal 10 mol % fluorobenzene. [b] In $CDCl_3$; δ in p.p.m. relative to internal $SiMe_4$. [c] From reference 2. [d] Partially obscured by dimethylglyoximate resonances. [e] Assumed values for the purposes of calculating σ_R^0. [f] Isomers in the ratio 2 : 1; major isomer assumed to be NCO, minor isomer OCN. [g] Only one isomer, assumed to be SCN, not NCS. [h] Made *in situ*. [i] 4-Fluorotoluene used as reference.

Only in a few cases were the identities of the complexes formed in doubt. These were as follows.

(*i*) L = $AsPh_3$. Even in the presence of a several-fold excess of triphenylarsine, under the conditions used complexing was incomplete and the resonances of the aqua-complex (9; L = OH_2) were still evident. However, since the chemical shifts for the triphenylarsine complex (9; L = $AsPh_3$) were not a function of the triphenylarsine concentration they are quoted in the Tables.

(*ii*) L = $[OH]^-$. Addition of $[AsPh_4][OH]$ to a solution of complex (9; L = OH_2) in methylene chloride gave an anionic complex which may have been either or both of the complexes (9; L = $[OH]^-$) or $[RhMe(dmg)(Hdmg)_2(OH_2)]$ in which one of the dimethylglyoximate ligands is deprotonated. As the character of this complex has not been studied in detail, the results for L = $[OH]^-$ must be treated with caution.

(*iii*) L = $[CNO]^-$. Two complexes were formed when $[AsPh_4][NCO]$ was added to complex (8; L = OH_2). Each complex had a separate ^{19}F n.m.r. resonance and doublet methylene-proton resonance, and a separate i.r. CN stretch band. In our studies of the cobaloxime series we also observed the two i.r. bands for the cyanato-complex,[2] although the ^1H n.m.r. spectrum showed only a single methylene resonance. We conclude that an equilibrium between cyanate and isocyanate complexes occurs in each case, but that it is established more rapidly in the case of the benzylcobaloxime complexes.

(*iv*) L = $[CNS]^-$. Only one complex was formed when an excess of $[AsPh_4][NCS]$ was added to each of the complexes (7)—(9) (L = OH_2). We have assumed, from a comparison of the i.r. spectra with those for the two complexes formed with the corresponding cobaloximes [2,3] (Table 5), that the ligand is bonded through sulphur to the rhodium.

---

* Due to coupling with ^{103}Rh nuclei.

(*v*) *Bridged complexes.* The formation of bridged dimeric complexes is discussed in more detail below.

Fluorine-19 *Resonances.*—In Table 2 are shown the ^{19}F chemical shifts of 11 anionic 4-fluorobenzyl- and six anionic 3-fluorobenzyl-rhodoximes, of corresponding fluorobenzylcobaloximes, some of which are from our earlier work,[2] of some neutral rhodoxime complexes, and of some related organic molecules and salts. The results show three interesting features: (*i*) the universally larger chemical shifts of the 4- than of the 3-fluorine substituents of the complexes; (*ii*) the wider range of chemical shifts of the 4-fluorine substituents in the rhodium complexes than in the cobalt complexes; and (*iii*) the very similar chemical shifts of the 3-fluorine substituents of the cobalt and rhodium complexes for each *trans* ligand.

The similarity of chemical shifts for the 3-fluorobenzyl-cobalt and -rhodium complexes for each particular *trans* ligand L (*e.g.* for L = $[CN]^-$ the shifts are 3.89 and 3.85 p.p.m., and for L = I^- they are 3.03 and 3.24 p.p.m., respectively) clearly indicates that, for each ligand L, the inductive effects of the substituents $[CH_2Co(Hdmg)_2L]^-$ and $[CH_2Rh(Hdmg)_2L]^-$ are almost identical. For these anionic complexes the inductive electron-donating effects are among the largest measured for any aromatic substituent. For example, the inductive substituent constant σ_I, calculated from equation (1),[8,*] ranges from —0.46 for the group $[CH_2Rh(Hdmg)_2(CN)]^-$ to —0.39 for $[CH_2Rh(Hdmg)_2I]^-$. This inductive effect

$$-\sigma_I = \left(\int_{H}^{3\text{-CH}_2\text{X}} - 0.60\right)\Big/7.10 \quad \text{(ref. 8)} \qquad (1)$$

$$\sigma_R{}^0 = \left(\int_{H}^{4\text{-CH}_2\text{X}} + 7.10\sigma_I - 0.60\right)\Big/(-29.5) \quad \text{(ref. 9)} \qquad (2)$$

is not solely the result of the field effect of the negative charge on the substituent, because: (*a*) the neutral rhodoxime substituent $CH_2Rh(Hdmg)_2(PPh_3)$ also has a large negative inductive substituent constant (σ_I = —0.34) which, like that for the corresponding substituent $CH_2Co(Hdmg)_2(PPh_3)$ is appreciably larger than that for the methyl group (σ_I = —0.08); and (*b*) the anionic group $[CH_2CO_2]^-$ ($[AsPh_4]^+$ as counter ion in the same solvent, CH_2Cl_2) has an inductive substituent constant of only —0.18 compared with 0.07 for the neutral substituent CH_2CO_2H.

Any field effect of the anionic charge is likely to be still less important when considering the difference between the chemical shifts of the 4- and 3-fluorine substituents. We ascribe the large differences between the chemical shifts of 4-fluorobenzyl- and 3-fluorobenzyl-rhodoximes to the hyperconjugative effect, the magnitude of which can be seen from the values of the resonance substituent constant $\sigma_R{}^0$ estimated using equation (2).[9] The values of $\sigma_R{}^0$ decrease markedly in the same sequence: L = $[CN]^- > [NO_2]^- > [N_3]^- \geqslant Cl^- \geqslant Br^- > [SCN]^- > I^-$ for both the rhodoximes and the cobaloximes. The greater influence of the rhodoxime substituent is evident from a plot of $\sigma_R{}^0$ for the rhodoximes against that for the cobaloximes (Figure 1). The greater the influence of the *trans* ligand the greater is the difference between the resonance substituent constants for the two metals. Similar conclusions about the overall electron-donating influence of the substituents $CH_2(Hdmg)_2L$ have been inferred from their effect on the ^{13}C chemical shifts of aromatic carbons in benzylcobaloximes.[10]

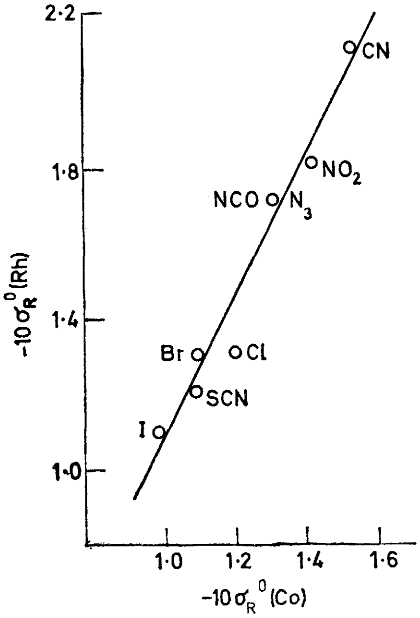


FIGURE 1 Plot of the resonance substituent constant $\sigma_R{}^0$ for the anionic substituents $[CH_2Rh(Hdmg)_2L]^-$ against that for the substituents $[CH_2Co(Hdmg)_2L]^-$ for several anionic ligands L

Comparison of the substituent constants of the rhodoximes and cobaloximes with those of the carbonyl-containing metallomethyl substituents such as $CH_2Fe(CO)_2(\eta\text{-}C_5H_5)$ suggests that the metalloximes are better inductive electron donors, although poorer hyperconjugative electron donors, than the latter substituents; only the substituent $[CH_2Rh(Hdmg)_2(CN)]^-$ approaches the hyperconjugative donor ability of the carbonyl-containing substituents. Whilst the use of fluorine chemical shifts as a measure of substituent effects has been criticised, our studies of equilibria [4] and reactivity [5] have confirmed the large electron-donating effects of the carbonyl-containing substituents. The similar effects of the methylmetalloxime substituents are likely therefor to be applicable to reactivity and equilibria, provided

---

[*] Equations (1) and (2) are reproduced as they appear in references 8 and 9. They are not integrals but the differences in fluorine chemical shifts of the 3-CH_2X-substituted and the unsubstituted compounds.

[8] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 709.

[9] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 3146.

[10] C. Bied-Charreton, B. Septe, and A. Gaudemer, *Organic Magnetic Resonance*, 1975, **7**, 116.

due account is taken of the fact that substituent effects measured from ^{19}F n.m.r. refer to interactions within a single molecule only, whereas those measured from rates and equilibria refer to a differential effect of the substituent on two states of the system.

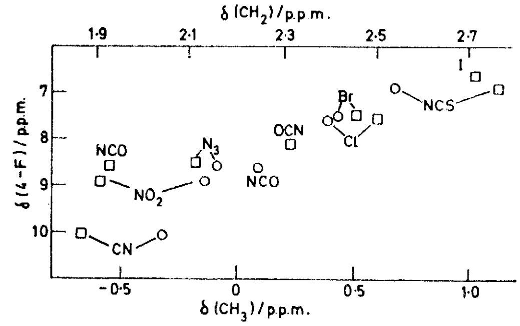


FIGURE 2 Plots of the upfield ^{19}F chemical shift of bis(dimethylglyoximato)(4-fluorobenzyl)ligandrhodium(III) complexes against the downfield proton chemical shifts for the methylene protons of the same molecules (□) and against the downfield ^1H chemical shifts for the methyl protons in corresponding bis(dimethylglyoximato)(ligand)methylrhodium(III) complexes (○)

Proton N.M.R. Spectra of Fluorobenzylrhodoximes.—The methylene proton resonances of the fluorobenzylrhodoximes are included in Table 2. As seen from Figure 2, a plot of $\delta(CH_2)$ against δ(4-F) is reasonably linear suggesting that the two properties are similarly influenced by the electronic perturbation caused by the *trans* ligand.

Bis(dimethylglyoximato)methylrhodium(III) *Complexes.*—(*a*) *Proton n.m.r. spectra.* The proton chemical shifts and coupling constants of (*ca.* 8%) carbon-13-enriched bis(dimethylglyoximato)methylrhodium(III) complexes (9) are shown in Table 3. For the anionic complexes, all prepared *in situ* from the aqua-complex, a plot of $\delta(CH_3)$, like that of $\delta(CH_2)$ for the fluorobenzyl complexes, is a near-linear function of the values of δ(4-F) (Figure 2).

TABLE 3

Proton chemical shifts of bis(dimethylglyoximato)methylrhodium(III) complexes [RhMe(Hdmg)$_2$L] and [AsPh$_4$]-[RhMe(Hdmg)$_2$L]

L	$\delta(CH_3)$ [a]	δ(Hdmg) [a]	J(C–H) [b]	J (Rh–H) [b]	J (P–H) [b]
[CN]$^-$	−0.31	1.97	134.1	2.1	
[CNCoMe]$^-$ [c]	−0.27	1.99			
[CNRhMe]$^-$	−0.22		134.4	1.9	
[NO$_2$]$^-$	−0.13	2.05	136.8	2.3	
[NCO]$^-$	−0.08	1.98	136.8	2.6	
[NCCoMe] [c]	0.02	2.02			
[NCRhMe] [c]	0.07		136.6	2.3	
[N$_3$]$^-$	0.10	2.07	137.0	2.5	
[OH]$^-$	0.09	1.93	138.2	2.5	
d	0.12	2.23		2.4	
Imidazole	0.17	2.15	135.6	2.4	
pyridine (py)	0.22	2.12	138.3	2.4	
P(OMe)$_3$	0.23	2.15	137.0	2.1	5.1
CNBu^t	0.23	2.19		2.1	
PBu$_3$	0.25	2.16	137.8	2.1	6.4
[S$_2$CNEt$_2$]$^-$ [e]	0.31	2.15	139.0	2.4	
4NC-py	0.38	2.15	137.3	2.5	
Cl$^-$	0.39	2.04	139.6	2.5	
Br$^-$	0.44	2.04	139.6	2.4	
NPhH$_2$	0.51	2.00	139.0	2.3	
AsPh$_3$	0.52	1.85	139.6	2.1	
OH$_2$	0.68	2.20	141.3	2.5	
[SCN]$^-$	0.69	2.18	139.4	2.2	
PPh$_3$	0.81	1.97	140.4	2.1	6.2

[a] ±0.05 p.p.m.; from SiMe$_4$. [b] ±0.2 Hz. [c] Bridged complexes CNCoMe = CNCoMe(Hdmg)$_2$, CNRhMe = CNRhMe(Hdmg)$_2$, *etc.* [d] 1,4-Diazabicyclo[2.2.2]octane. [e] [NEt$_2$H$_2$]$^+$ salt.

(*b*) *Carbon-13 n.m.r. spectra.* The ^{13}C n.m.r. spectra of the methylrhodoximes are shown in Table 4. All were measured in CH_2Cl_2–$CDCl_3$ mixtures without added SiMe$_4$ which would have obscured a number of the ^{13}C resonances. The variation of chemical shift of the methyl carbons is quite large, but no clear correlation

TABLE 4

Carbon-13 spectra of carbon-13-enriched bis(dimethylglyoximato)methylrhodium(III) complexes [RhMe(Hdmg)$_2$L] and [AsPh$_4$][RhMe(Hdmg)$_2$L]

L	$\delta(CH_3)$ [a]	δ[Hdmg(Me)] [a]	δ[Hdmg(C=N)] [a]	J(C–Rh) [b]	J(C–P) [b]
PBu$_3$	18.4	12.3	149.6	16.9	94.9
P(OMe)$_3$	16.2	11.8	148.8	17.7	132.4
PPh$_3$	14.3	12.3	150.8	19.1	75.0
AsPh$_3$	13.3	11.2	148.6	22.1	
OH$_2$	12.1	12.6	152.3	22.5	
[CN]$^-$	8.5	11.5	146.3	19.1	
[CNRhMe]$^-$ [c]	7.1	12.5	150.9	22.5	
[S$_2$CNEt$_2$]$^-$ [d]	5.8	12.4 or 11.0	149.2	22.1	
Br$^-$	5.0	12.5	150.0	23.5	
[SCN]$^-$	4.8	12.7	150.7	23.5	
[OH]$^-$	1.4	11.5	146.9	25.0	
Cl$^-$	1.4	12.2	149.8	25.0	
[NCO]$^-$	0.5	11.6	147.3	26.5	
Imidazole	0.3	12.0	149.5	22.1	
4NC-py	0.2	12.2	150.8	22.1	
NPhH$_2$	−0.2	11.9	146.3	22.1	
py	−0.6	11.9	149.2	23.5	
[NCRhMe]$^-$ [c]	−0.7	*e*	*e*	23.5	
[N$_3$]$^-$	−2.2	11.8	147.6	26.5	
[NO$_2$]$^-$	−3.3	11.8	147.2	23.5	

[a] ±0.4 p.p.m. from SiMe$_4$. [b] ±1.0 Hz. [c] Bridged complex (see text). [d] [NEt$_2$H$_2$]$^+$ salt. [e] Obscured.

with any other property of *trans* effects is apparent. The highest chemical shifts are for the ligands bonded through phosphorus and the lowest are for those bonded through nitrogen, particularly azide and nitrite. Whereas this is a similar order to that observed for ligand–metal *p*-orbital overlap and for the nucleophilicity of the same ligands toward Pt^{II}, other ligands such as water, which cause significantly large ^{13}C shifts, show no nucleophilicity to Pt^{II}.[11]

General Correlations.—In general, correlations between coupling constants and *trans* effects are more fruitful than correlation with chemical shifts.[12] Thus, a strongly bonding ligand is believed to decrease the coupling constant J(M–C–H) through a decrease in the *s* character of the C–M bond. Whilst such an approach is apparently effective in the case of platinum(II) complexes [13] for which there is a large variation in J(Pt–C–H), it is clearly unsuitable in this work because of the small values of J(Rh–C–H) (Table 3) and their still smaller changes with the nature of the *trans* ligand, which are little larger than the experimental errors. The values of J(C–H) are much larger, but show only a small variation which, for the anionic ligands $[CN]^-$ to I^-, parallels the chemical shifts of the α-protons and of the 4-fluorine nuclei, in the order $[CN]^-$ (134.4) < $[NO_2]^-$ (136.8) ⩽ $[NCO]^-$ (136.8) ⩽ $[N_3]^-$ (137.0) < $[SCN]^-$ (139.4) ⩽ Cl^- (139.6) < OH_2 (141.3 Hz). Clearly, the proton basicity of these anionic ligands is a major factor in determining the three properties [δ(α-H), δ(4-F), and J(C–H)] whereas π bonding plays little part. Similar proton-basicity correlations were found for the influence of neutral ligands, bonding through nitrogen, on the ^1H chemical shifts of methylcobaloximes.[14] On the other hand, some generalisations [6,7] about the relations between the chemical shifts of equatorial and axial ligands are not borne out by the present results. However, it is apparent from the results in Tables 3 and 4 that broad generalisations covering such a wide range of different ligand types are dangerous at the present time, until more is known of the factors determining chemical shifts and coupling constants.

Bridge Formation.—As demonstrated previously for the organocobaloximes,[2,3] bridged dimeric complexes were also formed from several of the anionic rhodoximes when there was a deficiency of the anionic ligand present, when the anionic complex was treated with 1 mol of an aqua-complex [equation (3)] or, in the case of the cyano-complexes, when the anionic complex was acidified [equations (4) and (5)]. These bridged complexes are readily detected in solution, either by the characteristic i.r. band [ν(CN) or ν(NN)] at a higher wavenumber (+19—35 cm^{-1}) than for the monomeric complexes (Table 5), or by the presence of two separate ^1H, ^{13}C, or ^{19}F n.m.r. resonances of equal intensity for each of the organic ligands of the bridged complex (Table 6) which are distinct from the single resonances of the monomeric complexes.*

$$[MR(Hdmg)_2L]^- + [M'R'(Hdmg)_2(OH_2)] \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} [(Hdmg)_2RMLM'R'(Hdmg)_2]^- \quad (3)$$

$$(M = Rh \text{ or } Co;\ M' = Rh \text{ or } Co;\ L = CN, SCN, \text{ or } N_3)$$

$$2[MR(Hdmg)_2(CN)]^- + [H_3O]^+ \rightleftharpoons [(Hdmg)_2RMCNMR(Hdmg)_2]^- + HCN \quad (4)$$

$$[(Hdmg)_2RMCNMR(Hdmg)_2]^- + [H_3O]^+ \rightleftharpoons [(Hdmg)(H_2dmg)RMCNMR(Hdmg)_2] \quad (5)$$

$$(M = Rh \text{ or } Co)$$

TABLE 5

Infrared spectra (cm^{-1}) of monomeric and bridged dimeric anionic complexes of the types (A) $[AsPh_4][RhR(Hdmg)_2L]$ and (B) $[AsPh_4][(Hdmg)_2RMLMR'(dmg)_2]$

				Band [a]	
Type	R	L	R′	M = Rh	M = Co
(A)	Me	CN		2 112	2 112
	$CH_2C_6H_4F$-4	CN		2 115	2 114
(B)	Me	CN	Me	2 139 [b]	2 148 [b]
	$CH_2C_6H_4F$-4	CN	$CH_2C_6H_4F$-4	2 141 [b] (2 140)	2 146 [b]
	$CH_2C_6H_4F$-4	CN	$CH_2C_6H_4F$-4	2 138 [c]	2 146 [c]
(A)	$CH_2C_6H_4F$-4	N_3		2 028	2 028
(B)	$CH_2C_6H_4F$-4	N_3	Me	2 043 [b]	2 049
(A)	$CH_2C_6H_4F$-4	SCN		2 097	2 094 [d]
(B)	$CH_2C_6H_4F$-4	SCN	$CH_2C_6H_4F$-4	2 132 [b]	2 129 [b]
(A)	$CH_2C_6H_4F$-4	NCO [e]		2 164	2 174
		OCN [e]		2 210	2 212

[a] ±2 cm^{-1}; measured in CH_2Cl_2. [b] Prepared *in situ*. [c] Protonated complex $[(H_2dmg)(Hdmg)RMCNMR(Hdmg)_2]$. [d] *S*-bonded isomer. [e] Assignment may be reversed.

A large number of bridged complexes may be prepared, containing the same or different metals and the same or different alkyl groups. The system is complicated by the fact that rearrangements and disproportionation [equations (6) and (7)] may take place.

$$[(Hdmg)_2RMCNM'R'(Hdmg)_2]^- \rightleftharpoons [(Hdmg)_2RMNCM'R'(Hdmg)_2]^- \quad (6)$$

$$2[(Hdmg)_2RMCNM'R'(Hdmg)_2]^- \rightleftharpoons [(Hdmg)_2RMCNMR(Hdmg)_2]^- + [(Hdmg)_2R'M'CNM'R'(Hdmg)_2]^- \quad (7)$$

The n.m.r. spectra in Table 6 therefore refer to the complexes formed initially in solution and not to those formed over longer periods.

The ^{19}F chemical shifts of Table 6 provide additional information about the character of the cobaloxime and rhodoxime bridges. For example, the 4-fluorine

---

* P. L. Gaus and A. L. Crumbliss (*Inorg. Chem.*, 1976, **15**, 739) have also shown that increased shielding of the cyanide carbon nucleus takes place on the formation of bridged cyano-complexes.

[11] U. Belluco, ' Organometallic and Coordination Chemistry of Platinum,' Academic Press, London, 1974, p. 148.

[12] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

[13] M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *Chem. Comm.*, 1971, 1627.

[14] C. Bied-Charreton, L. Alais, and A. Gaudemer, *Bull. Soc. chim. France*, 1972, 861.

chemical shift of the fluorobenzylrhodoxime attached to the carbon end of the cyano-bridge is more strongly decreased by co-ordination of a second rhodoxime [δ(F) 8.86 and 8.92 p.p.m.] than of a cobaloxime [δ(F) 9.4 and 9.5 p.p.m.] to the nitrogen end of the CN bridge [*cf.* δ(F) 10.06 p.p.m. for the monomeric cyano-complex]. Similarly, the fluorine chemical shift of the fluorobenzylrhodoxime at the nitrogen end of the CN bridge is larger [δ(F) 8.68 and 8.74 compared with 7.47 p.p.m.] when there is a cobaloxime than when there is a rhodoxime at the carbon end of the bridge. Clearly, the rhodoxime can not only transmit the *trans* effect of the ligand more readily than can the cobaloxime, as observed with the monomeric complexes, but it also makes greater demands on the complex attached to the other end of the bridge.

TABLE 6

N.m.r. spectra of bridged rhodoxime and cobaloxime complexes [a] of the types (D) $[AsPh_4][(Hdmg)_2RM'CNM''R''(Hdmg)_2]$ and (E) $[(Hdmg)(H_2dmg)R'M'CNM''R''(Hdmg)_2]$

Type	R′	M′	M″	R″	δ(F′) [b]	δ(F″) [b]	δ(H′) [c]	δ(H″) [c]
(D)	$CH_2C_6H_4F$-4	Rh	Rh	$CH_2C_6H_4F$-4	8.92	7.47	2.14	
(D) [d]	$CH_2C_6H_4F$-4	Rh	Co	$CH_2C_6H_4F$-4	9.40	6.74		
(D) [d]	$CH_2C_6H_4F$-4	Rh	Rh	Me	8.86			
(D) [d]	$CH_2C_6H_4F$-4	Rh	Co	Me	9.50			0.44
(D) [d]	Me	Co	Rh	$CH_2C_6H_4F$-4		8.74	0.53	
(D) [d]	$CH_2C_6H_4F$-4	Co	Rh	$CH_2C_6H_4F$-4	7.78	8.68		
(D) [d,e]	Me	Rh	Co	$CH_2C_6H_4F$-4		6.87		
(D) [d,f]	$CH_2C_6H_4F$-4	Co	Co	$CH_2C_6H_4F$-4	7.64	6.57		
(D) [d]	Me	Rh	Rh	Me			−0.22	0.07
(D) [d]	Me	Co	Rh	Me			0.53	0.02
(D) [d]	Me	Rh	Co	Me			−0.27	0.43
(D) [d,e]	Me	Co	Co	Me			0.54	0.45
(E) [h]	$CH_2C_6H_4F$-4	Rh	Rh	$CH_2C_6H_4F$-4	7.11	5.73	2.36	
(E) [g]	$CH_2C_6H_4F$-4	Rh	Rh	$CH_2C_6H_4F$-4	6.46	4.97		
(E) [g]	$CH_2C_6H_4F$-4	Rh	Co	$CH_2C_6H_4F$-4	6.39	3.37		
(E) [g]	$CH_2C_6H_4F$-4	Rh	Co	Me	6.50			
(E) [g]	$CH_2C_6H_4F$-4	Co	Rh	$CH_2C_6H_4F$-4	3.28	6.47		
(E) [g]	Me	Co	Rh	$CH_2C_6H_4F$-4		6.54		
(E) [g]	Me	Rh	Rh	Me			0.24	0.42

[a] In $CDCl_3$. [b] In p.p.m. relative to fluorobenzene. [c] In p.p.m. relative to $SiMe_4$. [d] Made *in situ* from aqua- and cyano-complexes. [e] From ref. 2. [f] $[NEt_4]^+$ salt. [g] Made *in situ* from complex type (D) and HBF_4. [h] With 20% (v/v) CD_3OD.

Formation Constants for Monomeric and Bridged Cyano-complexes.—Bridge formation presents an interesting problem in the determination of the formation constant of the monomeric cyano-complexes. In principle, provided that the concentration of the aqua- and bridged complexes is small compared with that of the monomeric cyano-complex, the formation constants can be determined in mildly alkaline solution by measuring the concentration of free cyanide ion, with a specific ion electrode, as a function of the concentration of the monomeric cyano-complex.

Thus, in aqueous solution, the formation constant for the monomeric complex is given by (8). If no bridging

$$K = [MR(CN)^-][CN^-][MR(OH_2)] \quad (8)$$

$$K_{app.} = [MR(CN)^-]/[CN^-]^2 \quad (9)$$

$$K_B = [RMCNMR^-]/[MR(CN)^-][MR(OH_2)] \quad (10)$$

occurs, $[CN^-] = [MR(OH_2)]$, but if bridging occurs, $[CN^-] > [MR(OH_2)]$ and the *apparent* equilibrium constant, derived from measurement of $[CN^-]$, is (9). The formation constant for the bridged complex is (10). When bridging occurs equation (11) is applicable, which, from equations (8) and (10), gives (12). Combining equations (9) and (12) we obtain (13).

$$[CN^-] = [MR(OH_2)] + [RMCNMR^-] \quad (11)$$

$$[CN^-] = \{[MR(CN)^-]/K[CN^-]\} + \{K_B[MR(CN)^-]^2/K[CN^-]\} \quad (12)$$

$$1/K_{app.} = (1/K) + \{K_B[MR(CN)^-]/K\} \quad (13)$$

A plot of $1/K_{app}$, determined using equation (9), against the concentration of the monomeric cyano-complex (≡ total complex present since there is little bridge formation) should therefore be linear with intercept $1/K$ and gradient K_B/K. Unfortunately, the

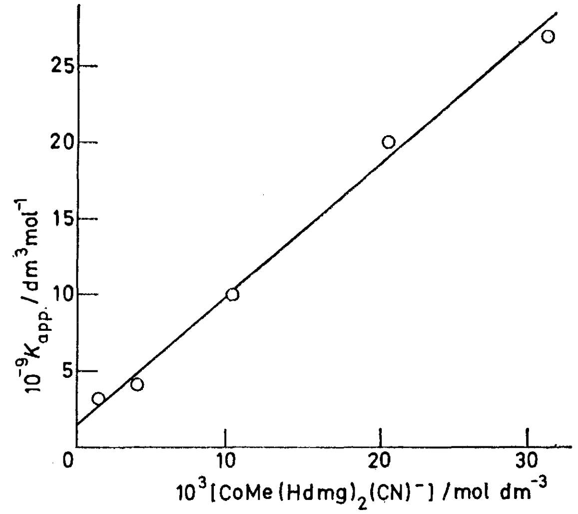


FIGURE 3 Plot of the apparent formation constant for μ-cyano-bis[bis(dimethylglyoximato)methylcobaltate(III)] [equation (9)] against the concentration of monomeric bis(dimethylglyoximato)(methyl)cyanocobaltate(III)

amount of free cyanide ion present in the solutions was much less than that predicted from the literature value of K (*ca.* 10^6 dm^3 mol^{-1}).[15] The determination therefore involved the use of the cyanide electrode in the lower limits of its range and only a lower limit to K can be obtained. Using aqueous buffers of pH 11.6 (a compromise between keeping cyanide ion from being protonated and the organometaloxime from being converted into its conjugate base), the plot in Figure 3 was obtained, giving $K \geqslant 5 \times 10^8$ dm^3 mol^{-1}. The formation constant for the bridged cyano-complex ($K_B \geqslant 5 \times 10^2$ dm^3 mol^{-1}) is comparable with that for other nitrogen ligands such as pyridine. A similar study of the rhodoxime complexes, which showed even lower cyanide-ion concentrations, was not pursued further.

EXPERIMENTAL

Materials.—Tetraphenylarsonium chloride hydrochloride, 3- and 4-fluorobenzylchloride, dimethylglyoxime, tributylphosphine, triphenylphosphine, trimethyl phosphite, triphenylarsine, 3- and 4-fluorophenylacetic acid, sodium azide, sodium cyanide, sodium thiocyanate, sodium cyanate, sodium chloride, sodium bromide, and sodium iodide were commercial materials used without further purification. Carbon-13-enriched (16%) methyl iodide (CEA France) was diluted two-fold with methyl iodide before use. Pyridine and aniline were redistilled before use. Diethylammonium diethylthiocarbamate was a gift from Dr. R. Crabtree. Tetraphenylarsonium salts of anionic ligands were prepared by the addition of a saturated solution of the sodium salt of the ligand (*e.g.* Na[CN]) to a neutralised saturated solution of $[AsPh_4]Cl\cdot HCl$ in warm water; the mixture was warmed to *ca.* 35 °C, cooled to 0 °C, and the crystals of the tetraphenylarsonium salt were filtered off, washed with ice-cold water, and dried *in vacuo*. Tetraphenylarsonium 3- and 4-fluorophenylacetate were prepared by the addition of tetraphenylarsonium hydroxide to a solution of 3- or 4-fluorophenylacetate in alkaline aqueous solution. The salt was extracted with methylene chloride, precipitated by the addition of diethyl ether, and dried *in vacuo*. 3-Fluorobenzyl-, 4-fluorobenzyl-, and carbon-13-enriched methyl-aquabis(dimethylglyoximato)rhodium(III) were prepared from the corresponding alkyl halide and dichloro(dimethylglyoxime)(dimethylglyoximato)rhodium(III) as described earlier.[1] The bridged complex tetraphenylarsonium μ-cyano-bis[bis(dimethylglyoximato)(4-fluorobenzyl)rhodate(III)] (Found: C, 48.0; H, 4.60; N, 9.85. $C_{55}H_{60}AsF_2N_9O_8Rh_2\cdot 1.3CH_2Cl_2$ requires C, 48.85; H, 4.55; N, 9.10%) was prepared by the addition of tetraphenylarsonium cyanide (1 mol) to $[Rh(CH_2C_6H_4F\text{-}4)(Hdmg)_2(OH_2)]$ (2 mol) in methylene chloride followed by precipitation with diethyl ether. Other tetraphenylarsonium bis(dimethylglyoximato)(4-fluorobenzyl)rhodate(III) complexes were prepared similarly[2] using 1 mol of the tetraphenylarsonium salt and 1 mol of $[Rh(CH_2C_6H_4F\text{-}4)(Hdmg)_2(OH_2)]$. Analyses are in Table 1.

N.M.R. Spectra.—Except where otherwise indicated in Table 2, the ^{19}F n.m.r. spectra were recorded using a Varian HA100 spectrometer with 10^{-4} mol complex in methylene chloride (0.5 cm^3) and 10 mol % fluorobenzene as internal standard. Samples were prepared by dissolving a known weight of the isolated complex in the solvent, by adding the tetraphenylarsonium salt of the appropriate anionic ligand (1.1 mol) to the aquabis(dimethylglyoximato)organorhodium(III) complex (1 mol) in methylene chloride, or by adding a neutral ligand (1.1 mol) to the rhodium(III) complex in methylene chloride. The ^1H n.m.r. spectra were recorded using a Varian A60 spectrometer and solutions prepared as for the fluorine spectra, above, but with $CDCl_3$ solvent. The ^{13}C n.m.r. spectra were obtained using a Brucker HX90 spectrometer and solutions prepared as above, but in the mixed solvent $CDCl_3$–CH_2Cl_2 (2 : 1 v/v, *ca.* 15 cm^3).

Determination of Formation Constants.—A known weight of tetrabutylammonium cyanobis(dimethylglyoximato)-methylcobaltate(III) (13—275 mg) was dissolved in 0.1 mol dm^{-3} aqueous sodium carbonate buffer (15 cm^3, pH 11.6) and the potential due to cyanide ion was measured with a specific cyanide electrode (EDT Supplies) as a function of time. After *ca.* 30 min, when the potential had reached a steady value, the cyanide-ion concentration was determined and the approximate formation constant $K_{app.}$ was calculated using equation (9). A calomel electrode was used as the reference with saturated ammonium nitrate as the salt bridge.

One of us (M. D. J.) thanks the Royal Society for a European Fellowship Award, and Dr. E. Lederer and his staff at I.C.N.S., C.N.R.S., Gif-sur-Yvette, France, for their hospitality during the tenure of the award.

[8/023 *Received, 6th January,* 1978]

---

[15] A. L. Crumbliss and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1970, **92**, 8.