Substituent Effects of (Transition Metallo)methyl Groups by Fluorine-19 Nuclear Magnetic Resonance

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A series of compounds of the general formula 3- and 4-$FC_6H_4CH_2ML_mL'_n$ where M is a transition metal have been synthesised and characterised. Ground state substituent effects of the metallomethyl groups $CH_2ML_mL'_n$ have been investigated by examination of the ^{19}F substituent chemical shifts (SCS). The results indicate that whilst these metallomethyl groups produce net electron donation to the aromatic ring, the magnitude of the effect is strongly dependent on the metal and its attached ligands. The substituent effects in these ground states are markedly smaller than those previously detected in transition states and in studies of equilibria, but the order of electron-donating ability within the series of metallomethyl groups is the same for the ground states and for the transition states and equilibria. The results show that several neutral (carbonyl)metallomethyl substituents are as electron donating as the most effective main group metallomethyl substituents, but the electron-donating character of several neutral cobalt(III)-containing substituents is little different from that of the methyl group. The analogous rhodium(III) substituents are markedly more electron donating.

RECENTLY there has been considerable evidence for and discussion of the large electron-donating effects of main group metallomethyl substituents such as CH_2SnMe_3 and $CH_2Hg{\cdot}CH_2Ph$. Evidence from electronic spectroscopy,[1] chemical reactivity data,[1] MO calculations,[2] and n.m.r. spectroscopy,[3] suggests that electron-releasing capacity of these groups can largely be attributed to hyperconjugation (also termed σ–π conjugation) between the metal and the organic group.

Most of these studies have concerned the Group IVB metalloids and mercury, but there is also some evidence that (transition metallo)methyl groups may have similar interesting electronic effects. Thus (i) the transition metal β-interaction [4] can be explained satisfactorily [1a] if the metallomethyl group $CR_2ML_mL'_n$ acts as a strongly electron-donating substituent. (ii) The substituent $CH_2Fe(CO)_2$-π-C_5H_5 is much more effective than is the methoxy-group in the promotion of electrophilic aromatic deuteriation [5] in the *ortho*- and *para*-positions. (iii) The substituent $CH_2Co(dmgH)_2py$ (where dmgH is the conjugate base of dimethylglyoxime) is more effective than is the methyl group, but less effective than is the methoxy-group in the promotion of electrophilic aromatic *para*-substitution by chlorine and bromine in acetic acid.[6] (iv) A study [7] of the influence of several $-CH_2ML_mL'_n$ groups (where M = Fe, Co, W, Mo, or Mn and L and/or L′ = carbon monoxide) on the acidity of pyridinium ions suggested that these groups are not only powerfully electron donating, but that this effect is also partially conjugative in origin.

However, effects such as (ii)—(iv) involve comparison of the electronic effect of the substituent in the ground state with its effect in a more demanding transition state, or comparison of the electronic effect of the substituent in two unequally demanding ground states. A knowledge of the corresponding electronic effect in a ground state alone would therefore be of particular interest.[8]

The ^{19}F shielding parameter of monosubstituted aryl fluorides has been shown to be a very sensitive criterion [9] of the electronic effect of substituents in the ground state. Substituents which are net electron donors enhance the electron density in the aromatic ring and hence cause shielding of the ^{19}F nucleus which is manifested in a positive substituent chemical shift (SCS) relative to the chemical shift of fluorobenzene. Substituents which withdraw electrons from the aromatic ring produce negative substituent chemical shifts. Dewar [10] has suggested that the extent to which a substituent perturbs the aromatic ring is reflected in the polarisation of the C–F bond, which involves orbitals largely concentrated on F. The extent of this polarisation is mainly determined by the π charge density at the carbon atom of the aromatic ring adjacent to the fluorine atom (I), excluding direct field effects. For electron-donating substituents, only 4-substituted fluoroaromatic compounds are believed to give unambiguous results; the SCS values for 3-substituted fluoroaromatics appear to be anomalous and difficult to interpret.[3a]

^{19}F SCS Data [3] have previously been used to investigate the ground-state effects of some main group metallomethyl substituents. In particular the observation that there is a stereoelectronic dependence of the orientation of the $CH_2ML_mL'_n$ group suggests that the electron-releasing character of these groups in the ground state is also mainly hyperconjugative in nature.

In this paper we describe and discuss studies of the

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[1] (*a*) T. G. Traylor, W. Hanstein, H. G. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, 1971, **93**, 5715 and references therein; (*b*) J. M. Jerkunica and T. G. Traylor, *ibid.*, p. 6278 and references therein; (*c*) C. G. Pitt, *Chem. Comm.*, 1971, 816; (*d*) M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **24**, 293.

[2] R. D. Bach and P. A. Scherr, *J. Amer. Chem. Soc.*, 1972, **94**, 220.

[3] (*a*) A. J. Smith, W. Adcock, and W. Kitching, *J. Amer. Chem. Soc.*, 1970, **92**, 6140; (*b*) W. Kitching, W. Adcock, S. Q. A. Rizvi, and A. J. Smith, *J. Organometallic Chem.*, 1972, **42**, 373; (*c*) A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **21**, 91.

[4] G. E. Coates, M. L. H. Green, and K. Wade, ' Organometallic Compounds,' Methuen, London, 1968, vol. II, p. 211 and references therein.

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

[6] S. N. Anderson, D. H. Ballard, and M. D. Johnson, *J.C.S. Perkin II*, 1972, 311.

[7] M. D. Johnson and N. Winterton, *J. Chem. Soc. (A)*, 1970, 507.

[8] M. J. S. Dewar, ' Hyperconjugation,' Ronald Press, New York, 1962.

[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**, 709, 3146.

[10] (*a*) T. G. Squires and M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1969, **91**, 379; (*b*) W. Adcock and M. J. S. Dewar, *ibid.*, 1967, **89**, 379.

^{19}F n.m.r. chemical shifts of a number of neutral 3- and 4-fluorobenzylmetal complexes containing (transition metallo)methyl substituents the same as, and related to, those concerned in previous studies.[5-7]

RESULTS

A series of fluorobenzyl(carbonyl)metal compounds was prepared and characterised. The analyses and ^{1}H n.m.r. and i.r. spectral characteristics are shown in Table 1. β-(4-Fluorophenyl)ethyl(dicarbonyl)-π-cyclopentadienyliron was also prepared and characterised.

A series of fluorobenzylbis(dimethylglyoximato)cobalt(III) complexes was prepared from the corresponding fluorobenzylbis(dimethylglyoximato)aquocobalt(III) complex. The characteristics of these compounds are shown in Table 2. In two cases the benzylcobaloximes were not isolated; instead a two-fold excess of the axial base (dimethyl sulphoxide and acetonitrile) was added to a suspension of the aquo-complex in warm methylene chloride until a homogeneous solution was obtained. The anionic complex 4-fluorobenzylbis(dimethylglyoximato)cyanocobaltate(III) was also prepared and isolated as the tetraethylammonium salt.

TABLE 1

Analyses, ^{1}H n.m.r., and i.r. characteristics of (fluorobenzyl)carbonylmetal compounds

Compound	Calc. (%) C	Calc. (%) H	Found (%) C	Found (%) H	N.m.r. data $\delta(CH_2)$ [a]	CO Stretching frequencies (cm^{-1}) [b]
$XFe(CO)_2$-π-C_5H_5 [f]	57·8	3·9	57·85	4·0	2·68	2009(s), 1952(s)
$XCH_2Fe(CO)_2$-π-C_5H_5	60·15	4·8	60·15	4·4	1·60, 2·68 [c]	2020(s), 1948(s)
$XMn(CO)_5$	47·4	2·0	47·5	2·05	2·28	2106(m), 2038(w,sh), 2013(vs), 1900(m,sh)
$XMn(CO)_4PPh_3$	65·25	4·0	65·9	4·2	1·67 [d]	2054(s), 1998(s), 1966(vs), 1944(s,sh)
$XMo(CO)_3$-π-C_5H_5	50·85	3·15	49·95	3·25	2·88	2019(s), 1936(s,sh), 1928(vs)
$XW(CO)_3$-π-C_5H_5	40·75	2·5	39·75	2·7	2·96	2018(s), 1932(vs), 1922(s,sh)
$XCo(CO)_3PPh_3$	65·4	4·1	64·9	4·25	3·33 [d]	2033(w), 1960(vs)

[a] $CDCl_3$ solution, relative to internal Me_4Si. [b] $CHCl_3$ solution; s = strong, sh = shoulder, m = medium, w = weak, v = very. [c] Two 'apparent' triplets. [d] Doublet, $J_{P\text{-}Mn\text{-}CH}$ 6 Hz. [e] Doublet, $J_{P\text{-}Co\text{-}CH}$ 2·5 Hz. [f] X = 4-$FC_6H_4CH_2$

TABLE 2

Analyses of organocobalt(III), organorhodium(III), and organoplatinum(II) complexes

Compound	Calc. (%) C	Calc. (%) H	Calc. (%) N	Found (%) C	Found (%) H	Found (%) N
$XCo(dmgH)_2H_2O$ [a]	43·25	5·3	13·45	43·5	5·35	13·3
$XCo(dmgH)_2SMe_2$	44·35	6·1	12·15	44·0	6·25	12·3
$XCo(dmgH)_2NMe_3$	47·25	6·35	15·3	47·0	6·4	15·35
$XCo(dmgH)_2NC_5H_5$	50·3	5·3	14·1	49·85	5·4	14·65
$XCo(dmgH)_2DMF$ [b]	45·85	5·75	14·85	45·7	5·8	14·75
$XCo(dmgH)_2PPh_3$	60·0	5·3	8·5	60·3	5·2	8·5
$XCo(dmgH)_2P(OMe)_3$	41·4	5·95	10·75	41·2	6·0	10·65
$XCo(dmgH)_2Bn$ [c]	51·15	5·05	16·3	51·05	5·15	16·35
$YCo(dmgH)_2SMe_2$ [d]	44·35	6·1	12·15	44·1	6·0	12·0
$YCo(dmgH)_2NC_5H_5$	47·25	6·35	15·3	46·95	6·3	15·0
$YCo(dmgH)_2PPh_3$	60·0	5·3	8·5	60·0	5·35	8·55
$YCo(dmgH)_2Bn$ [c]	51·15	5·05	16·3	51·0	5·1	16·2
$XRh(dmgH)_2NC_5H_5$	46·05	4·5	13·45	45·9	4·75	13·25
$XRh(dmgH)_2PPh_3$	56·2	4·95	7·95	56·0	4·9	8·0
$[XCo(dmgH)_2CN]NEt_4$	50·35	7·35	14·7	49·7	7·4	15·05
$[YCo(dmgH)_2CN]NEt_4$	50·35	3·35	14·7	50·15	7·2	14·5
$X_2Pt(PEt_3)_2$ [e]	48·05	6·45		47·7	6·5	

[a] X = 4-$FC_6H_4CH_2$. [b] DMF = *NN*-Dimethylformamide. [c] Bn = Benzimidazole. [d] Y = 3-$FC_6H_4CH_2$. [e] *cis*-Isomer.

Other new complexes prepared and characterised were 4-fluorobenzylbis(dimethylglyoximato)-triphenylphosphine- and -pyridine-rhodium(III), and *cis*-bis-(4-fluorophenyl)bis(triethylphosphine)platinum(II). Potassium 4-fluorobenzylpentacyanocobaltate(III) was prepared and recrystallised from aqueous methanol to give a fairly pure product, but potassium β-(4-fluorophenyl)ethylpentacyanocobaltate(III) could not be completely separated from iodopentacyanocobaltate(III) ion and was studied in the impure state. The characteristics of all these compounds are shown in Table 2.

^{19}F *N.m.r. Spectra.*—All the compounds were diamagnetic and give multiplet (AA′BB′X) fluorine resonances. In all cases only a single set of resonances could be detected despite the fact that it is probable that more than one species was present in solutions of the cobalt complexes. Most spectra were measured using two solvents, methylene chloride and *NN*-dimethylformamide (DMF). Little dissociation of the axial base from the cobaloximes is to be expected in methylene chloride, though some complexes are too insoluble in this solvent for reliable measurement of the chemical shifts to be made. In dimethylformamide, which is a more strongly co-ordinating solvent, some replacement of the axial base by the solvent undoubtedly occurs. In all cases, except those in which the solubility is very low, the concentration of the solutions used was 2·5 mole %. In the case of 4-fluorobenzyl(pyridine)-rhodoxime, a drop of methanol was added to the methylene chloride to facilitate solution. The pentacyanocobaltate(III) salts are insoluble in both organic solvents and the SCS values were recorded using aqueous solutions and an external reference. The spectrum of the 4-fluorobenzylcyanocobaloxime salt was measured in all three solvents. The SCS values of the compounds studied here and of some main group metal compounds, which are included for comparison, are shown in Table 3.

TABLE 3

^{19}F Substituent chemical shifts [a] (SCS) of substituted fluorobenzenes

(*a*) In methylene chloride and in dimethylformamide

Substituent	Chemical shift *para* CH_2Cl_2	*para* DMF [d]	*meta* CH_2Cl_2	*meta* DMF [d]
$CH_2Fe(CO)_2$-π-C_5H_5	+7·80	+7·93	+1·35 [b]	
$CH_2Mn(CO)_5$	+6·97	+7·30	+0·51 [b]	
$CH_2Mn(CO)_4PPh_3$	+8·56	+8·35	+1·62 [b]	
$CH_2Mo(CO)_3$-π-C_5H_5	+7·09	+7·14	+0·93 [b]	
$CH_2Co(CO)_3PPh_3$	+6·38	+5·97	+1·25 [b]	
$CH_2W(CO)_3$-π-C_5H_5	+7·27	+7·50		
$CH_2CH_2Fe(CO)_2$-π-C_5H_5	+5·42	+5·35		
$CH_2Co(dmgH)_2H_2O$	Insol	+5·41 [e]		
$CH_2Co(dmgH)_2DMSO$ [c]	+4·67			
$CH_2Co(dmgH)_2SMe_2$	+4·71	+5·02	+2·77	
$CH_2Co(dmgH)_2N{\equiv}CMe$	+4·79			
$CH_2Co(dmgH)_2NMe_3$	+4·80	+5·12		
$CH_2Co(dmgH)_2NC_5H_5$	Insol	Insol	+2·91	
$CH_2Co(dmgH)_2DMF$ [d]	+4·98	+5·44		
$CH_2Co(dmgH)_2PPh_3$	+4·97	+4·92	+2·97	
$CH_2Co(dmgH)_2P(OMe)_3$	+5·24	+5·19	+3·42	
$[CH_2Co(dmgH)_2CN]NEt_4$	+8·05	+8·50	+4·12	
$CH_2Rh(dmgH)_2NC_5H_5$	+6·71			
$CH_2Rh(dmgH)_2PPh_3$	+6·90			
$CH_2Pt(PEt_3)_2CH_2C_6H_4F$-*p* [f]	+4·52	+4·52		
CH_2SiMe_3		+7·20 [g]		+1·10 [g]
CH_2GeMe_3		+7·30 [g]		+1·10 [g]
CH_2SnMe_3		+8·15 [g]		+1·00 [g]
CH_2SiPh_3		+6·29 [h]		+1·12 [h]
CH_2HgCl		+6·80 [i]		+1·80 [i]
Et		+5·00 [h]		
Me	+5·58	+5·45		
OMe		+11·50		

(*b*) In water [j]

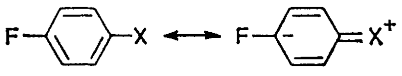
Substituent	*para*	*meta*
$[CH_2Co(CN)_5]^{3-}$	+7·84	
$[CH_2Co(dmgH)_2CN]^-Na^+$	+5·42	
$[CH_2Co(dmgH)_2CN]^-NEt_4^+$	+5·35	+2·21
$[CH_2CH_2Co(CN)_5]^{3-}3K^+$	+4·20	

[a] Relative to fluorobenzene (= 0) as internal reference. [b] From ref. 22. [c] DMSO = Dimethyl sulphoxide. [d] DMF = *NN*-Dimethylformamide. [e] H_2O base replaced by DMF. [f] *cis*-Isomer. [g] From ref. 3*a*. [h] From ref. 3*b*. [i] From W. Adcock, B. F. Hegarty, W. Kitching, and A. J. Smith, *J. Organometallic Chem.*, 1968, **12**, 21. [j] H_2O solvent, measured relative to fluorobenzene in a sealed capillary tube.

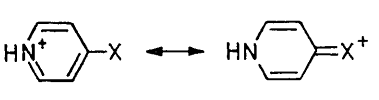
DISCUSSION

Inspection of Table 3 reveals large positive SCS values for the *para*-substituents $CH_2Fe(CO)_2$-π-C_5H_5, $CH_2Mn(CO)_4PPh_3$, $CH_2Mn(CO)_5$, $CH_2Co(CO)_3PPh_3$, $CH_2Mo(CO)_3$-π-C_5H_5, and $CH_2W(CO)_3$-π-C_5H_5. These values are very close to those observed for several main group metallomethyl substituents, and both sets of substituents have widely different effects when in the *meta*- and *para*-positions.[11] Thus it appears that these carbonyl(transition metallo)methyl substituents are of comparable electron-donating ability to the most effective of the main group substituents in the ground state.

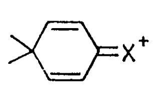
The replacement of the *trans*-C≡O ligand of the substituent $CH_2Mn(CO)_5$ by Ph_3P produces a large positive SCS (+1·59 p.p.m.; CH_2Cl_2), which is in accord with the stronger σ donor character and weaker π acceptor character of the triphenylphosphine ligand relative to carbon monoxide. The SCS values of these carbonyl containing $CH_2ML_mL'_n$ substituents show only slight solvent dependence. However, it is significant that the SCS values in DMF for all these substituents are appreciably less than that found for 4-fluoroanisole (SCS 11·5 p.p.m. in DMF). This shows that the (carbonyl)metallomethyl substituents are appreciably poorer electron donors than is the methoxy-group in the ground state of these compounds. Since, in the stabilisation of pyridinium ions [7] (II) relative to the corresponding pyridines and in the stabilisation of transition states for electrophilic aromatic substitution reactions [5] (III), these metallomethyl groups are much *more* effective than is the *p*-methoxy-group, it is apparent that these substituents are readily polarised and are appreciably polarisable *i.e.* the Hammett σ^+ constant relevant to structures such as (III) will be appreciably larger than the corresponding Hammett σ constant for each of these metallomethyl substituents.



(I)

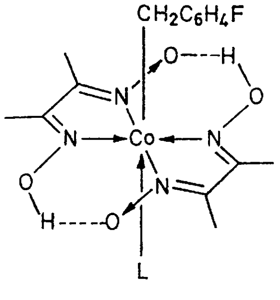


(II)



(III)

Such polarisation may explain the result of a study of the ^{19}F chemical shifts of pentafluorophenyl compounds,[12] which indicated that the *para*-substituent $CH_2Fe(CO)_2$-π-C_5H_5 has negligible electron-donating character. Whereas, in the 4-fluorophenyl derivatives the *para*-fluorine causes a small perturbation to the ring and evokes a weak response from the substituent, it is possible that in the pentafluorophenyl derivatives, the considerable interaction between the several fluorine substituents, particularly between *ortho*-fluorine atoms, greatly reduced the requirement for a response from the metallomethyl substituent.



(IV)

The effects of a number of substituents of the type $CH_2Co(dmgH)_2L$ (IV), where L is a neutral ligand *trans* to the methylene group and dmgH is the conjugate base of dimethylglyoxime *cis* to the methylene group, have also been examined. These compounds are of special

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[11] W. Adcock, S. Q. A. Rizvi, and W. Kitching, *J. Amer. Chem. Soc.*, 1972, **94**, 3657.

[12] M. I. Bruce, *J. Chem. Soc.* (*A*), 1968, 1459.

interest because they have been described extensively as models for vitamin B_{12} coenzyme, which also contains a metal–carbon bond of comparable character.[13] Little variation of the SCS values for the *para*-fluorine accompanies the change in the *trans*-ligand L in methylene chloride solution. The SCS values vary only slightly, from $+4{\cdot}67$ p.p.m. for L = dimethyl sulphoxide to $+5{\cdot}24$ for L = trimethyl phosphite, and little can be deduced about the ground state *trans*-effects of these ligands, though the order appears roughly to parallel ligand exchange rate studies [14] in which DMSO, MeCN, and Me_2S have been shown to exchange faster than PPh_3 and $P(OMe)_3$, an order which was considered to be consistent with the cobalt acting as a ' soft ' or ' class B ' acid. Addition of a ten-fold excess of Me_2S to the $CH_2Co(dmgH)_2SMe_2$ compound in CH_2Cl_2 produced no change in the SCS within experimental error ($\pm0{\cdot}05$ p.p.m.). The SCS values in DMF may represent population-averaged values but the difference between the SCS value for L = Me_2S in DMF and that for L = DMF in DMF suggest that even the relatively weakly co-ordinating Me_2S is not significantly displaced in DMF. On the other hand the similarity of the SCS values for L = H_2O and L = DMF in DMF suggest that the water is almost completely displaced by DMF. The range of SCS values for these substituents is similar to, or slightly less than, that observed for the methyl group, indicating that the $CH_2Co(dmgH)_2L$ substituents have comparable or slightly smaller electron-releasing ability than the methyl group in the ground state. Since the corresponding reactivity studies [6] showed that the methyl group is appreciably *less* electron donating than the group $CH_2Co(dmgH)_2L$, it is apparent that the latter is also appreciably polarisable.

However, whilst the SCS values of the $CH_2Co(dmgH)_2L$ group vary only slightly with change of the neutral ligand, substitution by the anionic cyanide ligand produces a dramatic increase in the *para*-SCS value (to $+8{\cdot}05$ p.p.m.; CH_2Cl_2). This represents a change in the SCS of *ca.* 3 p.p.m., signifying a large increase in electron-donating ability. The large effects of this and of other anionic ligands will be more fully discussed in a later paper.

The $CH_2Rh(dmgH)_2L$ substituents show much larger positive *para*-SCS values in CH_2Cl (*ca.* $+6{\cdot}8$ p.p.m.) than do their cobalt analogues, indicating that the former are much the more powerful electron-donating substituents; to an extent that they are comparable with the weaker carbonyl(transition metallo)methyl substituents. The increased positive SCS on going from the cobalt to the rhodium substituents is consistent with an increase in electropositivity of the metal, though more than one effect may be responsible for this difference. The greater electron-releasing ability of the $CH_2Rh(dmgH)_2L$ groups than of the analogous cobalt substituents is supported by chemical reactivity data, for the rhodium substituent has been shown to be more powerful than its cobalt analogue in the activation of the benzene ring to electrophilic attack by bromine.[15]

The neutral substituent *cis*-4-$FC_6H_4CH_2Pt(PEt_3)_2CH_2$ is also comparable with the methyl group in the ground state, but we have not yet investigated its effect in the transition state.

The SCS value of the anionic group $[CH_2Co(dmgH)_2CN]^-$ is very solvent dependent, increasing from $+5{\cdot}05$ in H_2O to $+8{\cdot}05$ p.p.m. in CH_2Cl_2. Since the latter value is larger than that of the (carbonyl)metallomethyl groups such as $CH_2Fe(CO)_2$-π-C_5H_5, it is probable that the ground-state electron-donating effect of the group $[CH_2Co(CN)_5]^{3-}$ (SCS $+7{\cdot}84$ p.p.m. in water) is also solvent dependent, and is very much greater than that of the carbonylmetal groups. Consequently, the order of electron donating ability in the ground state is $[CH_2Co(CN)_5]^{3-} > CH_2Fe(CO)_2$-$\pi$-$C_5H_5 > CH_2W(CO)_3$-$\pi$-$C_5H_5 \approx CH_2Mo(CO)_3$-$\pi$-$C_5H_5 \approx CH_2Mn(CO)_5 > CH_2HgCl$ which is the same as that previously determined for their effect on the acidity of 4-substituted pyridinium ions.[7] The latter effects are, however, appreciably larger than those observed here.

In the absence of stereochemical models to help us to distinguish between inductive and hyperconjugative electron release by these metallomethyl substituents, we have relied upon a comparison [3b,16] of the SCS values for the pairs of substituents $CH_2ML_nL'_m$ and $CH_2CH_2ML_nL'_m$. Whereas a fall in the SCS is to be expected when an extra methylene group is inserted between an inductively electron-donating substituent and the phenyl group,[17] the corresponding insertion of a methylene group between a (hyper)conjugatively electron-donating substituent and the phenyl group would be expected completely to remove the hyperconjugative effect between that substituent and the ring. On the assumption that the effects of methyl and ethyl groups are predominantly inductive, the fall in the SCS on changing from *para*-Me to *para*-CH_2Me ($5{\cdot}45$ to $5{\cdot}00$ p.p.m. in DMF) would indicate that there should be only a slightly larger fall-off on changing from *para*-$CH_2Fe(CO)_2$-π-C_5H_5 to *para*-$CH_2CH_2Fe(CO)_2$-π-C_5H_5. In fact the fall off in the latter cases is large, from $7{\cdot}93$ to $5{\cdot}35$ p.p.m. in DMF, *i.e. ca.* 2 p.p.m. larger and an additional effect must be very important, *i.e.* the hyperconjugative effect. Though the change in SCS on replacing *para*-Me by *para*-CH_2Me has not been determined in aqueous solution, it seems probable that the change from $7{\cdot}84$ to $4{\cdot}02$ p.p.m. observed on replacing *para*-$CH_2Co(CN)_5{}^{3-}$ by *para*-$CH_2CH_2Co(CN)_5{}^{3-}$ is also indicative of a hyperconjugative interaction. In these cases, the field effect may also be important. Such comparison of SCS values for 4-fluorobenzyl and β-(4-fluorophenyl)ethyl derivatives

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[13] D. Dodd and M. D. Johnson, *J. Organometallic Chem.*, in the press.

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has also been used to support the view that the hyperconjugative effect is important in compounds containing some main group metallomethyl substituents.[3b]

The similarity between the chemical shifts induced by the main group [3b,11] and (transition metallo)methyl substituents is evident in the values shown in Table 3, and the comparison with previous work suggests that the effects have a similar hyperconjugative origin. However, the range of values evident within the different sets of neutral (transition metallo)methyl substituents suggest that studies of the influence of the nature of the transition metal, of its oxidation state, of its charge, and of the ligands to which it is attached may provide valuable information about the nature of this hyperconjugative interaction.

EXPERIMENTAL

^{19}F *N.m.r. Spectra*.—The ^{19}F spectra were obtained with a Varian HA-100 spectrometer operating at 94·1 MHz, and at a temperature of 27 ± 2 °C. Solutions were generally 2·5 mole % of *p*-$FC_6H_4CH_2X$ (or saturated solutions if the compounds were not soluble to that extent), and contained 10 mole % fluorobenzene as an internal standard. The aqueous solutions were referenced to a capillary of fluorobenzene. The chemical shifts are accurate to ±0·05 p.p.m. Freshly prepared solutions were always used.

I.r. Spectra.—High resolution i.r. data were obtained using a Perkin-Elmer 257 grating spectrometer calibrated with air and polystyrene. The frequencies are accurate to ±1 cm^{-1}.

Materials.—Decacarbonyldimanganese (Strem Chemical Co.), bis(dicarbonyl-π-cyclopentadienyliron) (Alpha Inorganics), bis(dicarbonyl-π-cyclopentadienylmolybdenum) (Alpha Inorganics), octacarbonyldicobalt (Alpha Inorganics), 3- and 4-fluorobenzyl chloride (Emanuel), and β-(4-fluorophenyl)ethyl chloride (Emanuel) were commercial materials used without further purification. Bis(triphenylphosphine)-octacarbonyldimanganese was a gift from Dr. N. Winterton. Bis(tricarbonyl-π-cyclopentadienyl)tungsten was prepared from dicyclopentadiene (B.D.H.) and hexacarbonyltungsten (B.D.H.).[18]

Synthesis of Carbonylmetal Compounds.—3- and 4-Fluorobenzyl-dicarbonyl-π-cyclopentadienyliron(II),[19] -pentacarbonylmanganese(I),[20] -tricarbonyl-π-cyclopentadienylmolybdenum(II),[21] -tricarbonyl-π-cyclopentadienyltungsten(II), -tricarbonyltriphenylphosphinecobalt(I),[22] -tetracarbonyltriphenylphosphinemanganese(I),[23] and β-(4-fluorophenyl)ethyldicarbonyl-π-cyclopentadienyliron were prepared by standard methods previously described for the corresponding alkyl or benzyl derivatives from the corresponding sodium salt of the (carbonyl)metal anion and 3- or 4-fluorobenzyl chloride or β-(4-fluorophenyl)ethyl chloride, respectively, in tetrahydrofuran. The products were chromatographed on alumina and recrystallised from hexane. Analyses are shown in Table 2.

Synthesis of Cobaloximes.—3- and 4-Fluorobenzylbis(dimethylglyoximato)aquocobalt(III) was prepared by the reaction of 3- and 4-fluorobenzyl chloride with a solution of the bis(dimethylglyoximato)cobaltate(I) ion prepared from the base-catalysed disproportionation of bis(dimethylglyoximato)cobalt(II) in methanol.[6,18] All other 3- and 4-fluorobenzylbis(dimethylglyoximato)cobalt(III) compounds were prepared by the displacement of the axial water from the corresponding fluorobenzylbis(dimethylglyoximato)aquocobalt(III) compound by an excess of the appropriate ligand in acetone or chloroform. They were recrystallised from chloroform–light petroleum (b.p. 40—60°) or from aqueous acetone. Tetraethylammonium 4-fluorobenzylbis(dimethylglyoximato)cyanocobaltate(III) was prepared by heating a suspension of 4-fluorobenzylbis(dimethylglyoximato)aquocobalt(III) with an excess of sodium cyanide in aqueous solution until the former had all dissolved. After cooling, tetraethylammonium 4-fluorobenzylbis(dimethylglyoximato)cyanocobaltate(III) precipitated. The product was recrystallised from chloroform–light petroleum [ν_{CN} ($CHCl_3$) 2112 cm^{-1}].

Rhodoximes.—A solution of 4-fluorobenzylbis(dimethylglyoxime)methanolrhodium(III) was prepared by the reaction of 4-fluorobenzyl chloride with a methanolic solution of the bis(dimethylglyoximato)rhodium(I) ion which was obtained from the reduction of the dichloro(dimethylglyoxime)(dimethylglyoximato)rhodium(III) [24] with sodium borohydride under nitrogen.[25] 4-Fluorobenzylbis(dimethylglyoximato)-triphenylphosphine- and -pyridine-rhodium(III) were prepared by the addition of triphenylphosphine and pyridine, respectively, to the solution of the methanol complex. On partial evaporation of the methanolic solution the required complex precipitated out, and was recrystallised from chloroform–light petroleum (b.p. 40—60°).

Pentacyanocobaltates.—Potassium 4-fluorobenzyl- and β-(4-fluorophenyl)ethyl-pentacyanocobaltate(III) were prepared by the method of Halpern and Maher [26] from a two-fold excess of the pentacyanocobaltate(II) and the organic bromide and iodide, respectively. The solids obtained on evaporation of the reaction solutions and addition of ethanol were not purified but were used whilst still contaminated with the bromo(iodo)pentacyanocobaltate(III) salt.[27] The ^{1}H n.m.r. spectra of these complexes showed clearly the expected singlet (δ 2·87) and two triplet [δ 1·20 and 3·65 (*J* 7 Hz)] resonances in D_2O (relative to sodium 2,2-dimethyl-2-silapentanesulphonate).

cis-Bis-(4-fluorophenyl)bis(triethylphosphine)platinum(II) [28] was prepared from 4-fluorobenzylmagnesium chloride and dichlorobis(triphenylphosphine)platinum(II) in ether by the method of Chatt and Shaw,[29] and was recrystallised from aqueous methanol.

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