Infrared and Fluorine-19 Nuclear Magnetic Resonance Studies on σ-Phenyl–Transition Metal Complexes. Comments on the Nature of the Phenyl–Metal Bond

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Abstract: We have prepared a number of *m*- and *p*-fluorophenyl–transition metal complexes and measured their ^{19}F chemical shifts. These data, and chemical shift data from the literature for several fluorophenylplatinum compounds, were treated by the method of Taft, *et al.*, to obtain the inductive and resonance parameters σ_I and $\sigma_R{}^0$ for the metal substituent groups. The values determined for the resonance parameters were negative, implying that the metal group is a π-electron donor; these values varied over a small range, however, for rather different complexes, and in related series of compounds (*e.g.*, $Mn(CO)_{5-x}L_x$ or $Pt(PEt_3)_2X$) were almost invariant. The inductive parameters, however, varied greatly and in a predictable fashion. We conclude that strong emphasis must be placed on σ bonding between ligand and metal in the interpretation of these data, and that minor changes in $\sigma_R{}^0$ reflect the relative unimportance of π bonding to the ring relative to other ligands. We have observed a reasonable correlation between the ^{19}F chemical shift of *m*-$FC_6H_4CH_2X$ and group electronegativities, and from this can ascertain group electronegativities for organometallic groups. These values correlate with σ_I values. We have also reported carbonyl stretching frequencies for several *m*- and *p*-$XC_6H_4Mn(CO)_5$ complexes and find them nearly invariant to the nature or position of the substituent group on the ring. The relatively minor effect felt on the metal further substantiates our conclusion that π-bonding effects between ring and metal must be relatively inconsequential.

A rapid survey of the current organometallic literature is sufficient to assure one of the existence of an abundance of σ-bonded alkyl- and aryl–transition metal complexes.[1–4] Most of these complexes can be classified as "low-valent," with thermal stability attained by virtue of the presence of other ligands such as carbonyls, though, in fact, other alkyl and aryl complexes not falling into this categorization are becoming more familiar. As a general rule alkyls and aryls are considered as a single group; this is appropriate because of the often observed similarity of these compounds in terms of their preparations and properties including chemical reactivity and thermal stabilities.

Although there are apparent similarities between alkyl- and aryl–transition metal complexes, there is (conceptually at least) one difference between these two types of compounds. For metal–alkyl compounds, the metal–carbon bond is visualized as a σ bond only with no π-bond contribution.[5] For aryl–metal compounds the possibility exists for π bonding between metal and ring orbitals (π^*). Such an interaction would lead to charge delocalization from the metal to the ring and would enhance the metal–carbon bond order; this in turn would be expected to lend additional stability to the molecule.[6] In view of the general inclination toward back-bonding in low-valent complex chemistry, this interaction does look attractive, and indeed the suggestion of metal $\sigma + \pi$ bonding to aryl groups has considerable precedent in the literature. Its origin seems to be found in the work of Chatt and Shaw[7] on square-planar organo–nickel, –palladium, and –platinum complexes. For these complexes the qualitative order of thermal stability was explained by invoking metal–aryl π bonding and/or steric factors imposed by the ligands. Additional support for the occurrence of π bonding is found in proton nmr studies,[5,8] reactivity studies,[9] thermochemical data,[10] and esr measurements[11] on various phenyl–metal compounds, and from ^{19}F nmr data on monofluorophenyl-[9,12,13] and pentafluorophenyl–metal[14–17] compounds.

Recent X-ray crystallographic investigations on σ-phenyl and σ-pentafluorophenyl organometallic molybdenum[18,19] and nickel[20,21] complexes have purported to indicate substantial metal–aryl multiple bond-

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(1) R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1964).

(2) G. W. Parshall and J. J. Mrowca, *ibid.*, **7**, 157 (1968).

(3) R. J. Cross, *Organometal. Chem. Rev.*, **2**, 97 (1967).

(4) M. L. H. Green, "Organometallic Compounds," Vol. II, Methuen and Co. Ltd., London, 1968, pp 203–287.

(5) However, see J. D. Duncan, J. C. Green, M. L. H. Green, and K. A. McLauchlan, *Chem. Commun.*, 721 (1968).

(6) It is most generally assumed that the thermal decomposition of a compound will occur with cleavage of the weakest bond, which in the case of alkyl- and aryl–metal compounds is probably the metal–carbon bond. Hence a π interaction, between aryl ring and metal, which increases bond multiplicity and bond strength, should stabilize the aryl–metal complex over that of the corresponding alkyl compound. Some evidence suggests this is the case in some systems ($(phos)_2NiR_2$),[7] but in other instances ($RMn(CO)_5$) the difference is not so clear. Of course measurements of thermal stabilities (and chemical reactivities) are usually determined in a qualitative manner and often reported subjectively, so little emphasis can be placed on this line of reasoning.

(7) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705, 4020 (1959); 1718 (1960).

(8) H. C. Beachell and S. A. Butter, *Inorg. Chem.*, **4**, 1133 (1965).

(9) E. S. Bolton, G. R. Knox, and C. G. Robertson, *Chem. Commun.*, 664 (1969).

(10) S. J. Ashcroft and C. T. Mortimer, *J. Chem. Soc.*, *A*, 930 (1967).

(11) K. Matsuzaki and T. Yasukawa, *J. Organometal. Chem.*, **10**, P 9 (1967).

(12) G. W. Parshall, *J. Amer. Chem. Soc.*, **88**, 704 (1966).

(13) M. J. Church and M. J. Mays, *J. Chem. Soc.*, *A*, 3074 (1968).

(14) F. J. Hopton, A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *ibid.*, 1326 (1966).

(15) M. I. Bruce, *ibid.*, 1459 (1968).

(16) M. G. Hogben and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 283 (1969).

(17) M. G. Hogben, R. S. Gay, A. J. Oliver, J. A. J. Thompson, and W. A. G. Graham, *ibid.*, **91**, 291 (1969).

(18) M. D. Rausch, A. K. Ignatowicz, M. R. Churchill, and T. A. O'Brien, *ibid.*, **90**, 3242 (1968).

(19) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc.*, *A*, 1110 (1969).

(20) M. R. Churchill, T. A. O'Brien, M. D. Rausch, and Y. F. Chang, *Chem. Commun.*, 992 (1967).

(21) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc.*, *A*, 266, 2970 (1968).

Table I. Analytical Data for Compounds Prepared in This Work

			Analysis, calcd (found), %		
Compound	Color	Mp, °C[a]	C	H	Other
p-$\mathrm{FC_6H_4COMn(CO)_5}$	Yellow	93–94[b]	45.31 (46.21)	1.27 (1.60)	. . .
m-$\mathrm{FC_6H_4COMn(CO)_5}$	Yellow	88–89	45.31 (45.15)	1.27 (1.24)	. . .
p-$\mathrm{FC_6H_4Mn(CO)_5}$	White	65–67	45.54 (45.46)	1.39 (1.59)	Mn, 18.94 (16.49)
m-$\mathrm{FC_6H_4Mn(CO)_5}$	White	73–76	45.54 (45.64)	1.39 (1.76)	Mn, 18.94 (17.63)
p-$\mathrm{ClC_6H_4Mn(CO)_5}$	White	68–70[c]	43.10 (43.07)	1.32 (1.71)	Mn, 17.92 (17.51)
m-$\mathrm{ClC_6H_4Mn(CO)_5}$	White	80–84[d]	43.10 (45.06)	1.32 (1.35)	Mn, 17.92 (16.80)
p-$\mathrm{BrC_6H_4Mn(CO)_5}$	White	63–66[e]	37.64 (39.30)	1.15 (1.20)	Mn, 15.65 (15.55)
m-$\mathrm{BrC_6H_4Mn(CO)_5}$	White	56–58	37.64 (39.35)	1.15 (1.32)	Mn, 15.65 (15.38)
p-$\mathrm{CNC_6H_4Mn(CO)_5}$	White	120–122 d	48.51 (48.77)	1.36 (1.26)	Mn, 18.49 (17.03)
m-$\mathrm{CNC_6H_4Mn(CO)_5}$	White	82–84	48.51 (48.64)	1.36 (1.41)	Mn, 18.49 (16.60)
p-$\mathrm{CF_3C_6H_4Mn(CO)_5}$	White	74–75	42.38 (41.74)	1.18 (1.12)	Mn, 16.15 (16.12)
m-$\mathrm{CF_3C_6H_4Mn(CO)_5}$	White	44–45	42.38 (42.10)	1.18 (1.24)	Mn, 16.15 (16.42)
p-$\mathrm{FC_6H_4Mn(CO)_4P(C_6H_5)_3}$	Yellow	142–145 d	64.14 (64.42)	3.65 (3.70)	Mn, 10.48 (10.70)
m-$\mathrm{FC_6H_4Mn(CO)_4P(C_6H_5)_3}$	Gold	132–134 d	64.14 (64.48)	3.65 (3.80)	Mn, 10.48 (10.73)
p-$\mathrm{FC_6H_4Mn(CO)_4As(C_6H_5)_3}$	Yellow	134–137 d	59.18 (59.07)	3.37 (3.51)	Mn, 9.67 (9.51)
m-$\mathrm{FC_6H_4Mn(CO)_4As(C_6H_5)_3}$	Yellow	120–123 d	59.18 (59.09)	3.37 (3.71)	Mn, 9.67 (9.52)
p-$\mathrm{FC_6H_4Mn(CO)_4P(OC_6H_5)_3}$	White	69–71	58.76 (58.77)	3.35 (3.59)	. . .
m-$\mathrm{FC_6H_4Mn(CO)_4P(OC_6H_5)_3}$	White	65–67	58.76 (58.47)	3.35 (3.51)	. . .
p-$\mathrm{FC_6H_4Mn(CO)_4P(OC_2H_5)_3}$	White	39–40	44.88 (45.65)	4.47 (4.56)	. . .
m-$\mathrm{FC_6H_4Mn(CO)_4P(OC_2H_5)_3}$	White	53–54	44.88 (45.40)	4.47 (4.67)	. . .
p-$\mathrm{FC_6H_4Mn(CO)_3[P(OC_2H_5)_3]_2}$	White	39–41	44.53 (44.80)	6.05 (6.19)	. . .
m-$\mathrm{FC_6H_4Mn(CO)_3[P(OC_2H_5)_3]_2}$	White	37–38	44.53 (45.54)	6.05 (6.32)	. . .
p-$\mathrm{FC_6H_4COMn(CO)_3(diphos)}$	Yellow	156–158 d	65.46 (65.68)	4.27 (4.39)	Mn, 8.32 (8.22)
m-$\mathrm{FC_6H_4COMn(CO)_3(diphos)}$	Yellow	148–150	65.46 (65.15)	4.27 (4.52)	Mn, 8.32 (8.08)
p-$\mathrm{FC_6H_4Mn(CO)_3(bipy)}$	Red-orange	185–186 d	58.48 (58.09)	3.10 (3.12)	Mn, 14.08 (13.93)
m-$\mathrm{FC_6H_4Mn(CO)_3(bipy)}$	Red-orange	178–180 d	58.48 (58.04)	3.10 (3.20)	Mn, 14.08 (14.10)
p-$\mathrm{FC_6H_4Fe(CO)_2(\pi\text{-}C_5H_5)}$	Yellow-gold	60–62	57.39 (57.20)	3.33 (3.52)	. . .
m-$\mathrm{FC_6H_4Fe(CO)_2(\pi\text{-}C_5H_5)}$	Yellow-gold	39–41	57.39 (57.59)	3.33 (3.63)	. . .
p-$\mathrm{FC_6H_4NiP(C_6H_5)_3(\pi\text{-}C_5H_5)}$	Dark green	145–147 d	72.39 (72.03)	5.03 (5.30)	. . .
m-$\mathrm{FC_6H_4NiP(C_6H_5)_3(\pi\text{-}C_5H_5)}$	Dark green	107–111 d	72.39 (72.31)	5.03 (5.14)	. . .
m-$\mathrm{FC_6H_4CH_2Mn(CO)_5}$	Pale yellow	32–33	47.39 (47.30)	1.99 (1.98)	. . .
m-$\mathrm{FC_6H_4CH_2Mn(CO)_4P(C_6H_5)_3}$	Yellow-gold	166–169 d	64.70 (65.26)	3.93 (3.99)	. . .
m-$\mathrm{FC_6H_4CH_2Mn(CO)_4As(C_6H_5)_3}$	Gold	154–158 d	59.81 (58.59)	3.63 (3.57)	. . .
m-$\mathrm{FC_6H_4CH_2Mn(CO)_3(diphos)}$	Pale yellow	154 d	66.88 (64.64)	4.68 (4.49)	. . .
m-$\mathrm{FC_6H_4CH_2Fe(CO)_2(\pi\text{-}C_5H_5)}$	Yellow	51–52 d	58.78 (58.67)	3.88 (4.05)	. . .
m-$\mathrm{FC_6H_4CH_2Mo(CO)_3(\pi\text{-}C_5H_5)}$	Yellow	102–104 d	50.87 (50.24)	3.13 (2.92)	. . .
m-$\mathrm{FC_6H_4CH_2Co(CO)_3P(C_6H_5)_3}$	Yellow	. . .[f]	65.38 (65.21)	4.12 (4.22)	. . .
m-$\mathrm{FC_6H_4CH_2I}$	Red-orange liquid	. . .	35.62 (35.56)	2.56 (2.53)	. . .
m-$\mathrm{FC_6H_4CH_2OCH_3}$	Colorless liquid	. . .	68.56 (69.41)	6.47 (6.49)	. . .

[a] d = decomposes. [b] Lit. 94–95°, ref 36. [c] Lit. 70–71°, ref 37. [d] Lit. 80–82°, ref 38. [e] Lit. 65–66°, ref 37. [f] Decomposes at 131–139° without melting.

ing since the measured metal–carbon bond lengths are apparently shorter than those expected for a pure σ bond. Furthermore, it has been suggested[18] that the metal–aryl carbon distances in other aryl compounds of cobalt,[22] iron,[23] chromium,[24] rhodium,[25] tungsten,[26] and palladium[27] are probably significantly shorter than the corresponding metal–alkyl carbon distances as a result of the π-bonding contribution to the metal–carbon bond in the aryl complexes.

This work was initiated to further assess the role played by π bonding in the transition metal–aryl bond, with particular regard to its significance compared to metal–aryl σ bonding.

Experimental Section

Reagents. All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran was freshly distilled from lithium aluminum hydride; benzene was dried over calcium hydride. All other solvents (reagent grade) were used without further purification.

Substituted benzoyl chlorides were obtained from commercial sources with the exception of *m*-$\mathrm{NCC_6H_4COCl}$, which was prepared by the literature method.[28] Commercial samples of triphenylphosphine, triphenylarsine, tributylphosphine, triphenyl phosphite, trimethyl phosphite, triethyl phosphite, 2,2′-bipyridyl (bipy), $\mathrm{C_6H_5F}$, *m*-$\mathrm{FC_6H_4Br}$, *p*-$\mathrm{FC_6H_4Br}$, *m*-$\mathrm{FC_6H_4CH_3}$, *m*-$\mathrm{FC_6H_4CH_2Cl}$, and *m*-$\mathrm{FC_6H_4CH_2Br}$ were used as received. The method of Chatt and Hart[29] was used to prepare 1,2-bis(diphenylphosphino)ethane (diphos).

Manganese carbonyl was purchased commercially or was synthesized by the published method.[30] The following compounds were also obtained by published procedures: $\mathrm{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2}$,[31] $\mathrm{[(\pi\text{-}C_5H_5)Mo(CO)_3]_2}$,[32] and $\mathrm{(\pi\text{-}C_5H_5)NiP(C_6H_5)_3Cl}$.[33] Cobalt carbonyl was a commercial sample.

General. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim (Ruhr), West Germany, or by Galbraith Laboratories, Knoxville, Tenn. Melting points were determined on either a Kofler hot stage or a Thomas-Hoover

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(22) P. G. Owston and J. M. Rowe, *J. Chem. Soc.*, 3411 (1963).

(23) R. L. Avoyan, Yu. A. Chapovskii, and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 7, 900 (1966).

(24) J. J. Daly and R. P. A. Sneeden, *J. Chem. Soc., A*, 736 (1967).

(25) E. B. Fleischer and D. Lavallee, *J. Amer. Chem. Soc.*, **89**, 7132 (1967).

(26) V. A. Semion, Yu. A. Chapovskii, Yu. T. Struchkov, and A. N. Nesmeyanov, *Chem. Commun.*, 666 (1968).

(27) R. W. Siekman and D. L. Weaver, *ibid.*, 1021 (1968).

(28) M. Levine and R. Sedlecky, *J. Org. Chem.*, **24**, 115 (1959).

(29) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

(30) H. E. Podall and A. P. Giraitis, *J. Org. Chem.*, **26**, 2587 (1961).

(31) R. B. King, "Organometallic Syntheses," Vol. I, Academic Press, New York, N. Y., 1965, p 114.

(32) Reference 31, p 109.

(33) G. E. Schroll, U. S. Patent 3054815 (1962); *Chem. Abstr.*, **58**, 1494*c* (1963).

Table II. Infrared Carbonyl Stretching Frequencies[a]

Compound	Solvent	CO stretching frequencies, cm^{-1}
p-$FC_6H_4COMn(CO)_5$	$CHCl_3$	2111 (w), 2051 (w), 2006 (s), 1993 (w), 1606 (w)
m-$FC_6H_4COMn(CO)_5$	$CHCl_3$	2116 (w), 2051 (w), 2006 (s), 1996 (w), 1619 (w)
p-$FC_6H_4Mn(CO)_4P(C_6H_5)_3$	CCl_4	2063 (s), 1998 (s), 1981 (s), 1956 (s)
m-$FC_6H_4Mn(CO)_4P(C_6H_5)_3$	CCl_4	2063 (s), 1998 (s), 1983 (s), 1958 (s)
p-$FC_6H_4Mn(CO)_4As(C_6H_5)_3$	CCl_4	2066 (s), 1996 (s), 1981 (s), 1956 (s)
m-$FC_6H_4Mn(CO)_4As(C_6H_5)_3$	CCl_4	2065 (s), 2000 (s), 1984 (s), 1959 (s)
p-$FC_6H_4Mn(CO)_4P(n\text{-}C_4H_9)_3$	CCl_4	2058 (s), 1996 (s), 1970 (s), 1946 (s)
m-$FC_6H_4Mn(CO)_4P(n\text{-}C_4H_9)_3$	CCl_4	2056 (s), 1996 (s), 1972 (s), 1948 (s)
p-$FC_6H_4Mn(CO)_4P(OCH_3)_3$	CCl_4	2077 (s), 2007 (s), 1984 (s), 1962 (s)
m-$FC_6H_4Mn(CO)_4P(OCH_3)_3$	CCl_4	2075 (s), 2005 (s), 1990 (s), 1964 (s)
p-$FC_6H_4Mn(CO)_4P(OC_2H_5)_3$	CCl_4	2067 (s), 1997 (s), 1980 (s), 1958 (s)
m-$FC_6H_4Mn(CO)_4P(OC_2H_5)_3$	CCl_4	2071 (s), 2001 (s), 1986 (s), 1966 (s)
p-$FC_6H_4Mn(CO)_4P(OC_6H_5)_3$	CCl_4	2077 (s), 2012 (s), 1994 (s), 1975 (s)
m-$FC_6H_4Mn(CO)_4P(OC_6H_5)_3$	CCl_4	2081 (s), 2016 (s), 1996 (s), 1978 (s)
p-$FC_6H_4Mn(CO)_3[P(OC_2H_5)_3]_2$	CCl_4	2031 (w), 1946 (s), 1926 (sh)
m-$FC_6H_4Mn(CO)_3[P(OC_2H_5)_3]_2$	CCl_4	2032 (w), 1949 (s), 1930 (sh)
p-$FC_6H_4COMn(CO)_3$(diphos)	$CHCl_3$	1995 (s), 1920 (vs), 1596 (m)
m-$FC_6H_4COMn(CO)_3$(diphos)	$CHCl_3$	1996 (s), 1921 (vs), 1606 (w)
p-$FC_6H_4Mn(CO)_3$(bipy)	CH_2Cl_2	2000 (m), 1905 (s)
m-$FC_6H_4Mn(CO)_3$(bipy)	CH_2Cl_2	2000 (m), 1905 (s)
p-$FC_6H_4Fe(CO)_2(\pi\text{-}C_5H_5)$	CCl_4	2018 (s), 1973 (s)
m-$FC_6H_4Fe(CO)_2(\pi\text{-}C_5H_5)$	CCl_4	2020 (s), 1975 (s)
m-$FC_6H_4CH_2Mn(CO)_5$	$CHCl_3$	2102 (m), 2037 (w, sh), 2007 (s), 1992 (m)
m-$FC_6H_4CH_2Mn(CO)_4P(C_6H_5)_3$	$CHCl_3$	2050 (s), 2000 (s), 1970 (s), 1948 (s, sh)
m-$FC_6H_4CH_2Mn(CO)_4As(C_6H_5)_3$	$CHCl_3$	2051 (s), 2001 (s), 1976 (s), 1946 (s)
m-$FC_6H_4CH_2Mn(CO)_3$(diphos)	$CHCl_3$	1996 (s), 1923 (vs)
m-$FC_6H_4CH_2Fe(CO)_2(\pi\text{-}C_5H_5)$	$CHCl_3$	2015 (s), 1955 (s)
m-$FC_6H_4CH_2Mo(CO)_3(\pi\text{-}C_5H_5)$	$CHCl_3$	2017 (s), 1937 (vs)
m-$FC_6H_4CH_2Co(CO)_3P(C_6H_5)_3$	$CHCl_3$	2036 (w), 1964 (vs)

[a] Beckman IR-10 spectrometer.

capillary melting point apparatus and are uncorrected. These data are summarized in Table I.

Infrared Spectra. Routine infrared spectra were recorded on a Beckman IR-10 instrument and were calibrated with polystyrene (Table II). High-resolution infrared data were obtained with a Perkin-Elmer 421 grating spectrophotometer calibrated with CO and polystyrene (Table III). The latter values (cyclohexane solution) are believed accurate to ±1 cm^{-1}.

Table III. Carbonyl Stretching Frequencies of Substituted Phenylmanganese Pentacarbonyls

	Carbonyl stretching frequencies, cm^{-1} [a,b]		
Substituent	$A_1^{(2)}$	E	$A_1^{(1)}$
H[c,d]	2113	2017	1998
p-F[e]	2116	2020	2001
m-F	2117	2021	2000
p-Cl[f]	2117	2021	2001
m-Cl[g]	2117	2022	2000
p-Br	2116	2020	1999
m-Br	2117	2022	2000
p-CN	2119	2024	2000
m-CN	2119	2025	2000
p-CF_3	2118	2023	2000
m-CF_3	2118	2023	2000

[a] Cyclohexane solution. [b] Notation is that of ref 50. [c] Reference 54 gives 2114, 2021, and 1997 cm^{-1} (cyclohexane). [d] Reference 36 gives 2114, 2019, and 1997 cm^{-1} (heptane). [e] Reference 36 gives 2116, 2021, and 2000 cm^{-1} (heptane). [f] Reference 38 gives 2114, 2020, and 2003 cm^{-1} (cyclohexane). [g] Reference 38 gives 2116, 2026, and 2003 cm^{-1} (cyclohexane).

Fluorine Nuclear Magnetic Resonance. The ^{19}F nmr measurements were made at 26 ± 2° on a modified Varian HR-60 spectrometer operating at 56.4 MHz. Solutions containing 3–5 mol % FC_6H_4X or m-$FC_6H_4CH_2X$ were used. Fluorobenzene at approximately the same concentration was present as internal standard for the FC_6H_4X compounds, while external fluorobenzene was used as reference in the m-$FC_6H_4CH_2X$ series since in several cases the chemical shift lay close to that of the reference. Taft[34] has shown that the two methods are essentially equivalent for the concentrations used in this work. The spectra were calibrated with CF_3COOH, and chemical shifts are considered accurate to ±0.05 ppm. The ^{19}F chemical shifts (all relative to fluorobenzene) and other pertinent data are tabulated in Tables IV and V.

m- and p-$XC_6H_4COMn(CO)_5$ (X = H, F, Cl, Br, CN, CF_3). All of the benzoylmanganese pentacarbonyl complexes were prepared by similar methods in tetrahydrofuran or ether from $NaMn(CO)_5$ and the appropriate substituted benzoyl chloride.[35] The procedure for X = m-F is given below.

Manganese carbonyl (11.4 g, 29.2 mmol) was reduced with dilute sodium amalgam in 300 ml of anhydrous ether. After removal of excess amalgam the $NaMn(CO)_5$ solution was cooled to −20° and freshly distilled m-FC_6H_4COCl (11.3 g, 71.1 mmol) was added; the solution was then stirred for 1.5 hr. Removal of solvent at reduced pressure and below 20° gave a yellow-green solid residue which was extracted with dichloromethane–hexane. The solution was filtered and the filtrate concentrated at reduced pressure. After cooling to −78° yellow crystals (14.0 g, 75%) were collected on filtration. It is important that solutions of $XC_6H_4COMn(CO)_5$ be handled at <25° since decarbonylation occurs readily in ether or tetrahydrofuran to give $XC_6H_4Mn(CO)_5$ (see below).

m- and p-$XC_6H_4Mn(CO)_5$ (X = H, F, Cl, Br, CN, CF_3). The phenylmanganese pentacarbonyl complexes were prepared by thermal decarbonylation of the corresponding benzoyl compounds. A typical synthesis follows.

m-$FC_6H_4COMn(CO)_5$ (10.1 g, 31.8 mmol) was refluxed in 500 ml of ether for 5 hr. After evaporation of the solvent the pale yellow residue was crystallized from hexane at −78°, giving white crystals of m-$FC_6H_4Mn(CO)_5$ (7.95 g, 86%). Several of the benzoyl- and phenylmanganese pentacarbonyl complexes have been reported in the literature since this work was initiated.[36–38]

m- and p-$FC_6H_4Mn(CO)_4L$, and p-$FC_6H_4Mn(CO)_3L'_2$ (L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, P-

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

(35) T. H. Coffield, J. Kozikowski, and R. D. Closson, *J. Org. Chem.*, **22**, 598 (1957).

(36) K. Noack, U. Schaerer, and F. Calderazzo, *J. Organometal. Chem.*, **8**, 517 (1967).

(37) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. A. Ioganson, *Dokl. Akad. Nauk SSSR*, **175**, 1293 (1967).

(38) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. A. Ioganson, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 395 (1968).

Table IV. ^{19}F Nmr Parameters for FC_6H_4X Compounds

Substituent, X[a]	Solvent	δ_m[b]	δ_p[b]	σ_I	δ_R^0	Ref
$Mn(CO)_5$	CH_2Cl_2	+0.70	+7.63	−0.01	−0.24	*c*
	$CHCl_3$	+0.50	+7.31	+0.01	−0.23	*c*
	C_6H_{12}	+0.14	+7.25	+0.06	−0.24	*c*
$Mn(CO)_4P(C_6H_5)_3$	CH_2Cl_2	+2.08	+9.26	−0.21	−0.24	*c*
$Mn(CO)_4As(C_6H_5)_3$	CH_2Cl_2	+2.02	+9.01	−0.20	−0.24	*c*
$Mn(CO)_4P(OC_6H_5)_3$	CH_2Cl_2	+2.32	+9.20	−0.24	−0.23	*c*
$Mn(CO)_4P(OC_2H_5)_3$	CH_2Cl_2	+2.86	+9.78	−0.32	−0.23	*c*
$Mn(CO)_4P(OCH_3)_3$	CH_2Cl_2	+2.49	+9.48	−0.27	−0.24	*c*
$Mn(CO)_4P(n\text{-}C_4H_9)_3$	CH_2Cl_2	+2.63	+9.97	−0.29	−0.24	*c*
$Mn(CO)_3[P(OC_2H_5)_3]_2$	CH_2Cl_2	+4.89	+11.75	−0.60	−0.23	*c*
$NiP(C_6H_5)_3(\pi\text{-}C_5H_5)$	CH_2Cl_2	+3.71	+12.35	−0.44	−0.29	*c*
$Fe(CO)_2(\pi\text{-}C_5H_5)$	CH_2Cl_2	+2.37	+10.92	−0.25	−0.29	*c*
	. . .	+1.50	+10.23	−0.13	−0.30	*d*
trans-L_2PtCH_3	Acetone	+3.93	+11.70	−0.47	−0.26	*e*
	C_6H_{12}	+4.26	+11.70	−0.52	−0.25	*e*
trans-$L_2PtC_6H_5$	Acetone	+3.46	+10.90	−0.40	−0.25	*e*
	C_6H_{12}	+3.72	+10.90	−0.44	−0.24	*e*
trans-$L_2Pt(p\text{-}C_6H_4F)$	Acetone	+3.30	+10.80	−0.38	−0.25	*e*
	C_6H_{12}	+3.44	+10.80	−0.40	−0.25	*e*
trans-$L_2Pt(m\text{-}C_6H_4F)$	Acetone	+3.07	+10.60	−0.35	−0.26	*e*
trans-$L_2Pt(C{\equiv}CC_6H_5)$	Acetone	+3.21	+10.40	−0.37	−0.24	*e*
	C_6H_{12}	+3.37	+10.40	−0.39	−0.24	*e*
trans-L_2PtOCN	Acetone	+2.30	+10.10	−0.24	−0.26	*e*
	C_6H_{12}	+2.48	+10.20	−0.26	−0.26	*e*
trans-L_2PtCN	Acetone	+2.27	+9.32	−0.24	−0.24	*e*
	C_6H_{12}	+2.53	+9.11	−0.27	−0.22	*e*
trans-L_2PtCl	Acetone	+2.11	+10.10	−0.21	−0.27	*e*
	C_6H_{12}	+2.50	+10.20	−0.27	−0.26	*e*
trans-L_2PtBr	Acetone	+1.97	+9.86	−0.19	−0.27	*e*
	C_6H_{12}	+2.34	+10.00	−0.25	−0.26	*e*
trans-L_2PtI	Acetone	+1.56	+9.54	−0.14	−0.27	*e*
	C_6H_{12}	+2.00	+9.70	−0.20	−0.26	*e*
trans-L_2PtSCN	Acetone	+1.75	+9.29	−0.16	−0.26	*e*
	C_6H_{12}	+1.90	+9.20	−0.18	−0.25	*e*
trans-$L_2PtSnCl_3$	Acetone	−0.23	+6.96	+0.12	−0.24	*e*
cis-$L_2PtC_6H_5$	Acetone	+3.55	+11.60	−0.42	−0.27	*e*
cis-$L_2Pt(p\text{-}C_6H_4F)$	Acetone	+3.55	+11.60	−0.42	−0.27	*e*
cis-$L_2Pt(m\text{-}C_6H_4F)$	Acetone	+3.44	+11.20	−0.40	−0.26	*e*
cis-L_2PtCN	Acetone	+2.85	+9.48	−0.32	−0.22	*e*
cis-L_2PtCl	Acetone	+3.37	+9.75	−0.39	−0.22	*e*
trans-L_2PtCO^+	Acetone	−0.79	+4.56	+0.20	−0.18	*f*
	$CHCl_3$	−0.03	+4.30	+0.09	−0.15	*f*
trans-$L_2PtP(OC_6H_5)_3^+$	Acetone	−0.45	+5.38	+0.15	−0.20	*f*
	$CHCl_3$	+0.33	+4.92	+0.04	−0.16	*f*
trans-$L_2PtP(OCH_3)_3^+$	Acetone	+0.29	+6.36	+0.04	−0.21	*f*
	$CHCl_3$	+1.19	+6.00	−0.08	−0.16	*f*
trans-$L_2PtP(C_2H_5)_3^+$	Acetone	+0.39	+6.26	+0.03	−0.20	*f*
	$CHCl_3$	+1.37	+5.94	−0.11	−0.16	*f*
trans-$L_2PtCNC(CH_3)_3^+$	Acetone	+0.59	+6.84	0.00	−0.21	*f*
	$CHCl_3$	+1.59	+6.58	−0.14	−0.17	*f*
trans-$L_2Pt\text{-}(p\text{-}CH_3OC_6H_4NC)^+$	Acetone	+0.45	+6.62	+0.02	−0.21	*f*
	$CHCl_3$	+1.41	+6.30	−0.11	−0.17	*f*
$COMn(CO)_5$	CH_2Cl_2	−1.48	−3.64	+0.29	*g*	*c*
$COMn(CO)_3(diphos)$	CH_2Cl_2	+1.26	−0.36	−0.09	*g*	*c*

[a] L = $P(C_2H_5)_3$ for all Pt compounds. [b] Chemical shift in ppm relative to C_6H_5F. [c] This work. [d] Reference 9; solvent not given. [e] Reference 12. [f] Reference 13. [g] σ_R^0 not defined for $(\delta_p - \delta_m) < 0$.

Table V. ^{19}F Nmr Chemical Shifts in $m\text{-}FC_6H_4CH_2X$ Compounds

Substituent, X	$\delta(CH_2X)$[a]	Substituent, X	$\delta(CH_2X)$[a]
H	+1.18	OCH_3	+0.35
Cl	−0.58	$Mn(CO)_5$	+0.51
Br	−0.69	$Mn(CO)_4P(C_6H_5)_3$	+1.62
I	−0.74	$Mn(CO)_4As(C_6H_5)_3$	+1.53
CN	−1.21	$Mn(CO)_3(diphos)$	+1.74
COOH	−0.11	$Fe(CO)_2(\pi\text{-}C_5H_5)$	+1.35
$Si(CH_3)_3$	+1.23	$Mo(CO)_3(\pi\text{-}C_5H_5)$	+0.93
$N(CH_3)_2$	+0.88	$Co(CO)_3P(C_6H_5)_3$	+1.25
CH_3	+0.95		

[a] Chemical shift in ppm relative to $FC_6H_5\text{–}CH_2Cl_2$ solution.

$(OC_6H_5)_3$; L′ = $P(OC_2H_5)_3$, $^1/_2$bipy). Substitution reactions were carried out in refluxing dichloromethane (1,2-dichloroethane for L'_2 = bipy) using $FC_6H_4Mn(CO)_5$ and a stoichiometric amount of the ligand L or L′. Progress of the reaction was monitored by infrared spectroscopy. Solid complexes were purified by recrystallization from dichloromethane–hexane or dichloromethane–methanol and were identified by analysis and infrared spectra. The L = $P(n\text{-}C_4H_9)_3$ and L = $P(OCH_3)_3$ complexes were obtained as oils and could not be induced to crystallize. Solutions were filtered to remove suspended material and then solvent was removed at reduced pressure. These compounds were characterized by their infrared spectra and were not submitted for analysis. Similar substitution reactions have been described for $C_6H_5Mn(CO)_5$.[39-41]

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(39) W. D. Bannister, M. Green, and R. N. Haszeldine, *Chem. Commun.*, 54 (1965).

The low solubility of the two $FC_6H_4Mn(CO)_3(bipy)$ compounds prevented measurement of the ^{19}F nmr chemical shifts.

m- and p-$FC_6H_4COMn(CO)_3(diphos)$. Reaction of p-$FC_6H_4Mn(CO)_5$ (1.01 g, 3.45 mmol) and diphos (1.38 g, 3.47 mmol) in refluxing dichloromethane for 11 hr gave yellow crystalline p-$FC_6H_4COMn(CO)_3(diphos)$ which was recrystallized from dichloromethane–methanol (yield 2.02 g, 90%). A similar procedure afforded the *meta* compound. Both compounds show weak ketonic CO bands near 1600 cm^{-1} in their infrared spectra.

The benzoyl compound was also formed from p-$FC_6H_4Mn(CO)_5$ and diphos in dichloromethane at room temperature and in refluxing tetrahydrofuran. Unlike the $FC_6H_4COMn(CO)_5$ complexes the diphos-substituted derivatives were not decarbonylated in refluxing ether.

m- and p-$FC_6H_4Fe(CO)_2(\pi\text{-}C_5H_5)$. These compounds were prepared by a method analogous to that used for the preparation of the unsubstituted phenyl compound, $C_6H_5Fe(CO)_2(\pi\text{-}C_5H_5)$.[42] Synthesis of the *para* compound is described.

$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (4.70 g, 13.3 mmol) was reduced in tetrahydrofuran with dilute sodium amalgam. After removal of excess amalgam the $NaFe(CO)_2(\pi\text{-}C_5H_5)$ solution was cooled in Dry Ice. Freshly distilled p-FC_6H_4COCl (4.51 g, 28.6 mmol) was then added and the solution was stirred 2 hr at −78° followed by an additional 2 hr at room temperature. The product, p-$FC_6H_4COFe(CO)_2(\pi\text{-}C_5H_5)$, was isolated in the same manner as that described above for the $Mn(CO)_5$ analog (yield 5.97 g, 77%).

A solution of the benzoyl compound (3.19 g, 10.6 mmol) in 250 ml of tetrahydrofuran was irradiated in a quartz flask for 10 hr using a 140-W Hanovia ultraviolet source. Solvent was evaporated at reduced pressure and the residue was dissolved in benzene and chromatographed on alumina. The first band (bright yellow) was eluted with benzene and the solvent was removed, leaving a yellow-gold solid. This material was recrystallized from hexane at −78° to give 1.52 g (53%) of p-$FC_6H_4Fe(CO)_2(\pi\text{-}C_5H_5)$ as yellow-gold plates.

m- and p-$FC_6H_4NiP(C_6H_5)_3(\pi\text{-}C_5H_5)$. Reaction of FC_6H_4MgBr with $(\pi\text{-}C_5H_5)NiP(C_6H_5)_3Cl$ according to the literature procedure for the synthesis of the unsubstituted phenyl compound[43] afforded the dark green $FC_6H_4NiP(C_6H_5)_3(\pi\text{-}C_5H_5)$ complexes which were recrystallized from hexane–benzene.

m-$FC_6H_4CH_2Mn(CO)_5$. $NaMn(CO)_5$ was prepared as above from 6.85 g (17.6 mmol) of $Mn_2(CO)_{10}$ in 30 ml of tetrahydrofuran. m-$FC_6H_4CH_2Cl$ (6.00 g, 41.4 mmol) was added at room temperature and the resulting solution was stirred for 5 hr. Tetrahydrofuran was evaporated at reduced pressure and the solid was extracted with ether, filtered, and chromatographed on alumina. The product (pale yellow band) eluted first and the solution was concentrated and cooled in Dry Ice. Pale yellow crystalline m-$FC_6H_4CH_2Mn(CO)_5$ (7.80 g, 73%) was collected on filtration.

m-$FC_6H_4CH_2Mn(CO)_4P(C_6H_5)_3$. m-$FC_6H_4CH_2Mn(CO)_5$ (1.09 g, 3.58 mmol) and triphenylphosphine (0.97 g, 3.72 mmol) were refluxed in 200 ml of tetrahydrofuran for 54 hr. After evaporation of the solvent the residue was recrystallized from dichloromethane–hexane. Cooling to −78° deposited yellow crystals of the product which were isolated by filtration (yield 1.50 g, 78%).

m-$FC_6H_4CH_2Mn(CO)_4As(C_6H_5)_3$. This compound was prepared in 55% yield by the same method used above for the $P(C_6H_5)_3$ derivative.

m-$FC_6H_4CH_2Mn(CO)_3(diphos)$. Similar conditions to those directly above afforded this compound in 90% yield as pale yellow crystals.

m-$FC_6H_4CH_2Mo(CO)_3(\pi\text{-}C_5H_5)$. $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ (4.11 g, 8.40 mmol) was reduced with sodium amalgam in 100 ml of tetrahydrofuran. Excess amalgam was withdrawn and the $NaMo(CO)_3(\pi\text{-}C_5H_5)$ solution was cooled to 0°. m-$FC_6H_4CH_2Cl$ (2.87 g, 20.0 mmol) was added and after 1 hr of stirring the ice bath was removed; stirring was continued at room temperature for 72 hr. Solvent was removed at reduced pressure and the residue was dissolved in dichloromethane and filtered. The filtrate was chromatographed under nitrogen on alumina and the resulting bright yellow band was collected. Hexane was added; the solution was concentrated and cooled to −78°. Bright yellow crystals of m-$FC_6H_4CH_2Mo(CO)_3(\pi\text{-}C_5H_5)$ were collected on filtration (yield 3.32 g, 56%). The compound was stored under nitrogen in a refrigerator to prevent decomposition to a blue-green residue.

m-$FC_6H_4CH_2Fe(CO)_2(\pi\text{-}C_5H_5)$. $NaFe(CO)_2(\pi\text{-}C_5H_5)$ was prepared as above from 2.65 g (7.48 mmol) of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ in 100 ml of ether. m-$FC_6H_4CH_2Cl$ (2.70 g, 18.8 mmol) was added at −78° and the solution was stirred for 3 hr. After warming to room temperature the solution was filtered and then solvent was evaporated. The residue was dissolved in benzene and chromatographed on alumina. The product, which eluted first as a yellow-gold band, was collected and recrystallized from hexane (−78°) to give 1.69 g (39%) of fluffy yellow crystals.

m-$FC_6H_4CH_2Co(CO)_3P(C_6H_5)_3$. $NaCo(CO)_4$ was prepared by reducing $Co_2(CO)_8$ (2.17 g, 6.35 mmol) with sodium amalgam in ether (200 ml). Triphenylphosphine (3.38 g, 12.9 mmol) and m-$FC_6H_4CH_2Cl$ (2.35 g, 16.3 mmol) were then added at −78°. The solution was then warmed to 0° and stirring was continued for 60 hr at this temperature. Filtration, evaporation of ether, and recrystallization from dichloromethane–hexane (−78°) gave 3.66 g (55%) of m-$FC_6H_4CH_2COCo(CO)_3P(C_6H_5)_3$ as yellow crystals.

Refluxing an ether solution of m-$FC_6H_4CH_2COCo(CO)_3P(C_6H_5)_3$ (1.55 g, 2.86 mmol) for 6 hr and subsequent crystallization from dichloromethane–hexane (−78°) afforded 1.05 g (72%) of yellow crystalline m-$FC_6H_4CH_2Co(CO)_3P(C_6H_5)_3$.

m-$FC_6H_4CH_2I$. Sodium iodide (11.9 g, 79.4 mmol) and m-$FC_6H_4CH_2Cl$ (5.93 g, 41.2 mmol) were refluxed in anhydrous acetone for 1.5 hr. The solution was filtered to remove NaCl and solvent was evaporated from the filtrate to give an orange liquid and a white solid (excess NaI and some NaCl). Ether was added, followed by water, and the ether layer was separated and dried over Na_2SO_4. After removal of ether the remaining orange liquid was distilled at 15 mm to give 7.66 g of crude product, bp 80–87°. This sample was redistilled to give 5.08 g (52%) of red-orange m-$FC_6H_4CH_2I$, bp 88° (15 mm). The compound is an *extremely* powerful lachrymator and should be handled accordingly.

m-$FC_6H_4CH_2OCH_3$. Anhydrous methanol (10 ml) was added with stirring to sodium methoxide (4.23 g, 78.5 mmol) and m-$FC_6H_4CH_2Cl$ (9.04 g, 62.3 mmol) giving an exothermic reaction. The mixture was refluxed 1.5 hr and then cooled to room temperature. Water was added to dissolve any solid material and the solution was extracted with ether. After separation and drying (over Na_2SO_4) of the ether layer, the solution was distilled at 15 mm to give 7.20 g (83%) of the colorless product, bp 115–118°.

Other m-$FC_6H_4CH_2X$ Compounds. The m-fluorobenzyl compounds with X = CH_3,[34] CN,[34] COOH,[34] $Si(CH_3)_3$,[44] and $N(CH_3)_2$[45] were synthesized by methods outlined in the literature.

Results and Discussion

Preparative Methods. The presence of four carbonyl stretching frequencies in the infrared spectra of the $FC_6H_4Mn(CO)_4L$ and m-$FC_6H_4CH_2Mn(CO)_4L$ compounds indicates a *cis* configuration. This configuration is also found in monosubstituted derivatives of $C_6H_5Mn(CO)_5$ and $CH_3Mn(CO)_5$.[39–41] The infrared spectra of the two $FC_6H_4Mn(CO)_3[P(OC_2H_5)_3]_2$ compounds suggest a mutual *trans* arrangement of phosphite ligands, the same geometry found in bis(phosphite) derivatives of $C_6H_5Mn(CO)_5$.[39–41] The $FC_6H_4COMn(CO)_3(diphos)$, $FC_6H_4Mn(CO)_3(bipy)$, and m-$FC_6H_4COMn(CO)_3(diphos)$ complexes appear to have a *mer* arrangement of the three carbonyl groups by analogy with $C_6H_5Mn(CO)_3(diphos)$.[39,40] A *trans* configuration is assigned to m-$FC_6H_4CH_2Co(CO)_3P(C_6H_5)_3$ by comparison to $C_6H_5CH_2Co(CO)_3P(C_6H_5)_3$.[46]

In general the compounds in this work were synthesized by methods which parallel those used to prepare similar compounds. Pertinent literature references have been cited previously, and it should also be added that the related compounds $C_6H_5CH_2Mn(CO)_5$,[47]

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(40) W. D. Bannister, B. L. Booth, M. Green, and R. N. Haszeldine, *J. Chem. Soc., A*, 698 (1969).

(41) B. L. Booth, M. Green, R. N. Haszeldine, and N. P. Woffenden, *ibid.*, 920 (1969).

(42) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 2, 15 (1964).

(43) H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida, and N. Hagihara, *ibid.*, 6, 86 (1966).

(44) R. W. Bott, C. Eaborn, and B. M. Rushton, *ibid.*, 3, 448 (1965).

(45) F. N. Jones and C. R. Hauser, *J. Org. Chem.*, 27, 4020 (1962).

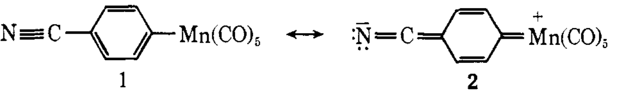
(46) Z. Nagy-Magos, G. Bor, and L. Markó, *J. Organometal. Chem.*, 14, 205 (1968).

$C_6H_5CH_2Fe(CO)_2(\pi\text{-}C_5H_5)$,[48] and $C_6H_5CH_2Mo(CO)_3(\pi\text{-}C_5H_5)$[49] are known. Therefore, except for the anomalies discussed below, the synthetic work will not be discussed further.

Reaction of $m\text{-}FC_6H_4Mn(CO)_5$ and 2 equiv of $P(OC_6H_5)_3$ in refluxing dichloromethane (60 hr) still afforded only the monosubstituted derivative $m\text{-}FC_6H_4Mn(CO)_4P(OC_6H_5)_3$ in about 50% yield. This contrasts with the results observed for $C_6H_5Mn(CO)_5$ and the same ligand.[39-41] With an excess of this ligand in dichloromethane (20°) only the *disubstituted* products $C_6H_5COMn(CO)_3L_2$ (50%) and $C_6H_5Mn(CO)_3L_2$ (10%) were formed. In tetrahydrofuran (20°) both $C_6H_5COMn(CO)_4L$ and $C_6H_5COMn(CO)_3L_2$ are formed when 2 equiv of ligand are used; $C_6H_5COMn(CO)_4L$ is the product when 1 equiv of $P(OC_6H_5)_3$ is used. If benzoyl compounds are formed as intermediates in our substitution reactions, they are certainly decarbonylated under much less severe conditions than those needed for $C_6H_5COMn(CO)_4L$ and $C_6H_5COMn(CO)_3L_2$.[41]

Bannister, *et al.*,[39,40] report the formation of $C_6H_5Mn(CO)_3$(diphos) by reacting $C_6H_5Mn(CO)_5$ and the ligand in dichloromethane at 20°. Under the same conditions we observed formation of the *benzoyl* compound when $p\text{-}FC_6H_4Mn(CO)_5$ was used as starting material. In addition, the benzoyl compound resulted when the reaction was carried out in refluxing dichloromethane or refluxing tetrahydrofuran. Both *m*- and $p\text{-}FC_6H_4COMn(CO)_3$(diphos) exhibit weak ketonic carbonyl bands near 1600 cm^{-1}, which could easily be overlooked; conclusive evidence for the *benzoyl* formulation is obtained from the ^{19}F nmr chemical shifts (Table IV). Comparison of these values with the corresponding chemical shifts of $Mn(CO)_5$, $COMn(CO)_5$, $Mn(CO)_4L$, and $Mn(CO)_3L'_2$ substituents indicates the presence of the acyl carbonyl group between the fluorophenyl ring and the manganese moiety. The differences observed in the reactions of $FC_6H_4Mn(CO)_5$ and $C_6H_5Mn(CO)_5$ are apparently due to the presence of the fluorine substituent on the phenyl ring in the former compounds.

Infrared Spectra of *m*- and $p\text{-}XC_6H_4Mn(CO)_5$. If a π interaction exists between the metal and phenyl ring in transition metal–phenyl systems then this interaction should be increased by *ortho* or *para* ring substitution of groups which withdraw electron density from the ring by a resonance mechanism. Thus for $p\text{-}NCC_6H_4Mn(CO)_5$ one would expect resonance structures such as **2** below to contribute significantly and lead to enhanced π delocalization over that in the corresponding *m*-CN derivative or in the unsubstituted compound.



1 2

Any substantial changes in the π-acceptor ability of the phenyl ring should influence the electron density at the metal and hence lead to changes in the three infrared-active carbonyl stretching frequencies of the $Mn(CO)_5$ group, with a more pronounced effect on the $A_1^{(1)}$ mode associated primarily with the unique *trans* carbonyl.[50-53]

In order to test this idea a series of *meta*- and *para*-substituted phenylmanganese pentacarbonyl compounds, $XC_6H_4Mn(CO)_5$ (X = H, F, Cl, Br, CN, CF_3), was synthesized and their infrared spectra were recorded. The carbonyl stretching frequencies for these compounds are presented in Table III.[54] It is surprising to find that the $A_1^{(1)}$ ν(CO) mode in all 11 compounds is practically invariant to both the nature of the substituent X and to its position on the ring; indeed, the range of values for the $A_1^{(1)}$ mode is only 3 cm^{-1}. Slightly greater deviations are observed for the $A_1^{(2)}$ and E modes, but the differences are still not large enough to show a definite trend. The observation that anticipated variation in manganese–phenyl π bonding in $XC_6H_4Mn(CO)_5$ compounds due to *meta* or *para* ring substitution cannot be detected from the carbonyl stretching frequencies contrasts with similar studies on a series of $XC_6H_4Fe(CO)_2(\pi\text{-}C_5H_5)$ compounds.[9] These studies revealed linear correlations for the two carbonyl stretching frequencies with the appropriate Hammett substituent constants. The differences in ν(CO), however, were relatively small ($\sim$12 cm^{-1}).

We would choose to interpret these data to indicate that the net charge delocalization to the phenyl ring is rather small, compared with the charge delocalization to the carbonyls, which are acknowledged to be good back-bonding ligands. Major changes on the ring would have only a minor effect on the electron density at the metal, if this assumption is right, and hence there would be little change in ν(CO). The slightly larger effect in $\pi\text{-}C_5H_5Fe(CO)_2C_6H_4X$ is probably a result of the presence of only two CO groups *vs.* five in the manganese compound; the two carbonyls would be forced to respond to a greater extent and appear more sensitive to the net electron density change.

^{19}F Nmr Studies of *m*- and $p\text{-}FC_6H_4X$ Compounds. A much more sensitive probe than carbonyl stretching frequencies for investigating transition metal–aryl π bonding is provided by ^{19}F nmr in the cases where the aryl group is *m*- or $p\text{-}FC_6H_4$. Taft and coworkers[34,55-57] have published extensive data on the ^{19}F nmr shielding in *meta*- and *para*-substituted fluorobenzenes, FC_6H_4X, which allow the separation of inductive (σ_I) and resonance ($\sigma_R{}^0$) effects of the substituent group X. The inductive (or polar) parameter σ_I measures the relative ability of the substituent to withdraw or release electron density both through space and the σ-bond system of the benzene ring.[58] Similarly $\sigma_R{}^0$ is a measure of the relative ability of the substituent to withdraw or release electron density by a resonance interaction with the benzene π system.[58] The substituent X = H is used as reference with the values $\sigma_I = \sigma_R{}^0 = 0$ given by definition.

The two substituent parameters for a particular group X are related to the ^{19}F chemical shifts (ppm relative to

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(47) R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).

(48) J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, **88**, 4862 (1966).

(49) R. B. King and A. Fronzaglia, *ibid.*, **88**, 709 (1966).

(50) F. A. Cotton and C. S. Kraihanzel, *ibid.*, **84**, 4432 (1962).

(51) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

(52) F. A. Cotton, *ibid.*, **3**, 702 (1964).

(53) W. A. G. Graham, *ibid.*, **7**, 315 (1968).

(54) The carbonyl stretching frequencies were assigned according to J. B. Wilford and F. G. A. Stone, *ibid.*, **4**, 389 (1965).

(55) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 3146 (1963), and references therein.

(56) J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *ibid.*, **90**, 5236 (1968).

(57) P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, **6**, 147 (1968).

(58) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **79**, 1045 (1957).

FC_6H_5) in m-FC_6H_4X (δ_m) and p-FC_6H_4X (δ_p) by eq 1 and 2.[34,55] A positive σ_I (σ_R^0) value indicates that X is

$$\delta_m = -7.10\sigma_I + 0.60 \qquad (1)$$

$$\delta_p - \delta_m = -29.5\sigma_R^0 \qquad (2)$$

electron withdrawing by an inductive (resonance) mechanism with respect to hydrogen.

The method of Taft was originally extended to transition metal substituents by Parshall,[12] who studied the bonding in fluorophenylplatinum complexes of the type *cis*- and *trans*-$[P(C_2H_5)_3]_2PtRY$ (R = m- or p-FC_6H_4; Y = one-electron donor ligand). More recently, additional ^{19}F nmr data have been published for various platinum,[13] mercury,[59-61] copper,[62] and iron[9] compounds.

The ^{19}F nmr parameters obtained in this work are tabulated in Table IV together with other related values from the literature. It is immediately obvious from the signs of σ_I and σ_R^0 that while transition metal substituents may either withdraw or release electrons by an inductive mechanism, they are invariably π-electron donors to the fluorophenyl ring (relative to hydrogen). The latter conclusion was also reached in the previous ^{19}F nmr studies.[9,12,13]

The inductive parameter (σ_I) varies considerably with ligand substitution in these same three series.[63] The more positive σ_I values for the cationic platinum substituents compared with those for the analogous neutral derivatives would be anticipated intuitively because of the presence of a formal positive charge on the metal.[64] At the same time, the variation of σ_I in a series of derivatives related by substitution, *e.g.*, $Mn(CO)_5$ (σ_I = −0.01), $Mn(CO)_4P(OC_2H_5)_3$ (σ_I = −0.32), and $Mn(CO)_3[P(OC_2H_5)_3]_2$ (σ_I = −0.60) (all CH_2Cl_2) appears to be regular and in the direction predicted on the basis of electronegativities. So also are the smaller differences observed between related complexes of the same formula and stoichiometry; *e.g.*, *cis*-$Mn(CO)_4L$, L = $P(C_6H_5)_3$, σ_I = −0.21; L = $P(OC_6H_5)_3$, σ_I = −0.24. The same variation is clearly seen in the series of complexes *trans*-$Pt[P(C_2H_5)_3]_2X$ in which σ_I varies from +0.12 (X = $SnCl_3$) to −0.52 (X = CH_3); one can choose other complexes from Table IV and draw a similar parallel. The surprising feature of Table IV is the approximate constancy of σ_R^0 in each of the following three related series of metal substituent groups regardless of the ligands bonded to the metal atom: (1) $Mn(CO)_5$, $Mn(CO)_4L$, and $Mn(CO)_3L'_2$, σ_R^0 = −0.23 to −0.24 (CH_2Cl_2); (2) L_2PtY, σ_R^0 = −0.22 to −0.27 (acetone) or −0.22 to −0.26 (C_6H_{12}); (3) $L_2PtL'^+$, σ_R^0 = −0.18 to −0.21 (acetone) or −0.15 to −0.17 ($CHCl_3$). One can assume that substitution of a ligand L for CO (in, for example, $FC_6H_4Mn(CO)_5$) leads to a higher negative charge on the metal; this is certainly suggested by the variation in σ_I. This in turn would raise the d orbital energy levels and should lead to more π bonding to the ligands including the phenyl group. The lack of variation in σ_R^0 indicates that there is little change in back-bonding to the phenyl ring, however. This would seem to indicate that the back-bonding to the carbonyl goups (being highly effective electron sinks) simply predominates and that the phenyl ring really sees very little net change as a result. This is the idea which we felt best explained our infrared data for X–$C_6H_4Mn(CO)_5$, so in that sense we see the infrared and nmr data as complementary.

The small variation in σ_R^0, either on change of Y or on change of geometry, for the $[P(C_2H_5)_3]_2PtY$ substituents is particularly interesting. Parshall[12] argues from the chemical shift values that in these complexes the extent of π delocalization to the fluorophenyl ring depends on the nature of the group *trans* to the aryl ring; *i.e.*, there is a smaller degree of platinum → ring back-bonding if Y = CN or $SnCl_3$ than if Y = Cl, Br, or I in the *trans* derivatives. However, one must question the mathematical significance of his calculated "π acceptor parameters," which are differences between two relatively large numbers.[64] Subsequent work has led to the conclusion that relative ligand π acceptor strengths cannot be ascertained by the Parshall method.[12]

It is remarkable that the Taft resonance parameter (σ_R^0) does not vary substantially (−0.22 to −0.29) for the entire series of 27 neutral metal substituents since one or more of the following factors is altered throughout the series:[65] (1) the metal atom, (2) the coordination geometry, and (3) the ligands bonded to the metal atom. Slightly more positive σ_R^0 values (poorer π donor ability) of the cationic platinum substituents are not unexpected as a result of the formal positive charge,[67] but the difference is remarkably small. The much larger relative change (+0.12 to −0.60) in the inductive parameter (σ_I) suggests that in these compounds the *inductive* effects are dominant in the transition metal–aryl bond.[68] Thus although ^{19}F nmr measurements provide evidence for transition metal → aryl π donation, the magnitude of σ_R^0 implies that these metal substituents donate π-electron density to the fluorophenyl ring with an ability intermediate between that of $OCOCH_3$[55] (σ_R^0 = −0.21) and OC_6H_5[55] (σ_R^0 = −0.31). The degree of this interaction remains practically invariant to the nature of the metal group primarily as a consequence of the great acceptor ability of the other ligands (*vs.* C_6H_5) to compensate. This constancy of σ_R^0 argues strongly for the π interaction being small and of little consequence in terms of stabilization of the complex, contrary to earlier implications; one would hardly visualize σ_R^0 values being insensitive to the nature of the metal substituent if it were large. It is somewhat interesting to speculate on the existence of possible systems in which the back-bonding to a phenyl group might be of some consequence. Most likely such systems, if

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(59) W. Adcock, B. F. Hegarty, W. Kitching, and A. J. Smith, *J. Organometal. Chem.*, **12**, 21 (1968).

(60) W. Kitching, W. Adcock, and B. F. Hegarty, *Aust. J. Chem.*, **21**, 2411 (1968).

(61) V. S. Petrosyan and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **180**, 876 (1968).

(62) A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 2168 (1968).

(63) The relatively large solvent dependence of σ_I (and to a lesser extent σ_R^0) for the cationic platinum groups is undoubtedly the result of increased solvent–solute and/or solute–solute interactions; *cf.* ref 34.

(64) A similar trend is illustrated by σ_I parameters for organic substituents: NH_2 (−0.03), NH_3^+ (+0.60); $N(CH_3)_2$ (+0.10), $N(CH_3)_3^+$ (+0.92); CH_2NH_2 (+0.04), $CH_2NH_3^+$ (+0.26); data calculated from ref 34 in methanol.

(65) These factors are extremely important in the case of organophosphorus substituents, *e.g.*, ref 56 and 66.

(66) A. W. Johnson and H. L. Jones, *J. Amer. Chem. Soc.*, **90**, 5232 (1968).

(67) For organic substituents *cf.* CH_2NH_2 (σ_R^0 = −0.09) and $CH_2NH_3^+$ (σ_R^0 = −0.01); data from ref 34 and 55 in methanol.

(68) Similar conclusions were recently obtained for phosphorus–aryl bonds in organophosphorus compounds of the type $FC_6H_4PR_2X$.[66]

they were to exist, would avoid the conventional *low-valent* ligands (CO, phosphines); instead ligands like bipyridine or phenyl itself would have to be the only ones present. Certainly some effort should be directed to synthesis of complexes to test this hypothesis.

It is appropriate to observe that the data on fluorophenyl- and chlorophenyl-transition metal complexes seems complementary to the point of view expressed here. It is well established that enhanced thermal and oxidative stability is observed with substitution on the ring of electronegative groups such as fluorine[69–71] or chlorine.[71] These groups are of course π donating but strongly electron withdrawing by an inductive mechanism. Indeed if π bonding were significant, the substitution of fluorine should have a destabilizing effect. The inductive effect strongly predominates, however; enhancement of stability then results from an inductive withdrawal of electron density from the metal with a simultaneous increase in ionic resonance energy of the metal–carbon bond.[6,7] This is akin to saying that the σ bond is stabilized, so stabilizing the molecule as a whole.

^{19}F Nmr Study of *m*-$FC_6H_5CH_2X$ Compounds. Since transition metal–aryl bonding appears to be dominated by inductive effects, it would be useful to obtain relative group electronegativities of various metal substituents such as those in the above ^{19}F nmr studies. Group electronegativities of many common groups (alkyl, alkoxy, amino, *etc.*) have been determined by a wide variety of methods,[72] most of which are not easily extended to metal groups.

We have observed an empirical linear relationship between the ^{19}F nmr chemical shift, $\delta(CH_2X)$, in substituted *m*-fluorobenzyl derivatives, *m*-$FC_6H_4CH_2X$, and the group electronegativity, $\chi(X)$, of the substituent X.[73] The correlation is shown in Figure 1 for the ten organic substituents investigated. A least-squares analysis of the data gives

$$\delta(CH_2X) = -2.29\chi(X) + 6.15 \qquad (3)$$

The electronegativity correlation resulting from this method is at least as good as that obtained by other techniques[72] and has the added feature of being readily applicable to transition metal substituents. Using eq 3 and the measured ^{19}F nmr chemical shifts (Table V), relative group electronegativities have been calculated for seven metal groups. These data are shown in Table VI along with the Allred–Rochow and Pauling electronegativities of the free metal atoms. In all cases the calculated values are higher than those of the metal atoms, a result which is hardly surprising. Removal of electron density from the metal by back-bonding to the ligands should increase the effective electronegativity over that of the free metal atom. Moreover, since $P(C_6H_5)_3$ is both a poorer π acceptor and a better σ donor than CO,[50–53] the group electronegativity of $Mn(CO)_4P(C_6H_5)_3$ would be expected to be lower than that of $Mn(CO)_5$. This is, of course, the trend observed.[74]

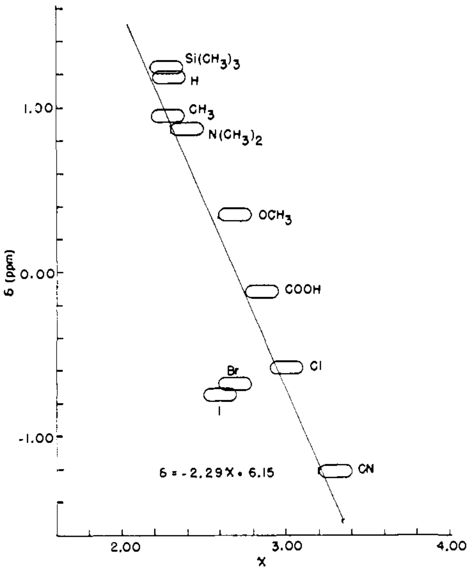

Figure 1. Least-squares plot: ^{19}F chemical shift (δ) in *m*-$FC_6H_4CH_2X$ compounds *vs.* electronegativity (χ) of substituent X.

Table VI. Group Electronegativity Values for Metal Substituents

Substituent	χ, calcd[a]	—χ, metal atom— A-R[b]	P[c]
$Mn(CO)_5$	2.47	1.60	1.55
$Mn(CO)_4P(C_6H_5)_3$	1.98	1.60	1.55
$Mn(CO)_4As(C_6H_5)_3$	2.02	1.60	1.55
$Mn(CO)_3$(diphos)	1.93	1.60	1.55
$Fe(CO)_2(\pi\text{-}C_5H_5)$	2.10	1.64	1.83
$Mo(CO)_3(\pi\text{-}C_5H_5)$	2.28	1.30	2.16
$Co(CO)_3P(C_6H_5)_3$	2.14	1.70	1.88

[a] Calculated from eq 3. [b] Allred–Rochow value; see ref 81, p 103. [c] Pauling value; see ref 81, p 103.

Relative group electronegativity values obtained from ^{19}F nmr chemical shifts in *m*-fluorobenzyl–transition metal complexes thus appear to agree with what would be expected on an intuitive basis, at least for the limited number of compounds investigated. Whether one prefers to use the term "group electronegativity" and the values calculated by eq 3, simply the chemical shifts themselves, or subsequently derived σ_I parameters for the CH_2X groups is of little consequence since the trends revealed are the same in any case. Obviously the method should be extended to include other transition metal substituents.

Conclusions

There can be no doubt that π delocalization from a transition metal to a σ-bonded aryl ring does occur.

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(69) R. D. Chambers and T. Chivers, *Organometal. Chem. Rev.*, **1**, 279 (1966).

(70) P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 146 (1964).

(71) M. D. Rausch, Y. F. Chang, and H. B. Gordon, *Inorg. Chem.*, **8**, 1355 (1969), and references therein.

(72) For an excellent summary, see P. R. Wells, *Progr. Phys. Org. Chem.*, **6**, 111 (1968).

(73) Group electronegativity values used are those tabulated by J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965), except for X = CN and COOH which are not included in this compilation. The values for CN (3.30) and COOH (2.85) were taken from ref 72.

(74) Saito, *et al.*,[75] have calculated an electronegativity value for nickel in the complex $bipyNi(C_2H_5)_2$ from nmr chemical shift values for methyl and methylene protons; the value found was ~1.9, close to the Pauling value of 1.8. This result is anticipated by our observations here. The electronegativity value is a function of the ligand; it approaches the Pauling value when phosphines replace CO (*viz.* $Mn(CO)_5$, $\chi = 2.47$; $Mn(CO)_4L$, $\chi \approx 2.0$; $Mn(CO)_3$diphos, $\chi = 1.93$; *vs.* Pauling value of 1.55). Qualitatively this is interpreted by assuming that the electronegativity (*i.e.*, ability to attract electrons) is strongly enhanced by ligands like CO which withdraw electrons from the metal.

(75) T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji, and S. Ikeda, *J. Amer. Chem. Soc.*, **88**, 5198 (1966).

However, the extent to which this interaction is significant *in these systems* appears to be small and of secondary importance compared to metal–aryl σ bonding,[76] in contrast to previous suggestions.[5,7,9,12,18–21] We therefore feel that arguments based on thermal stabilities of transition metal–aryl compounds (relative to the analogous alkyl derivatives) or on shortened metal–carbon bond distances[77] are without adequate support. It is possible, however, under certain circumstances involving metal–aryl complexes with ligands of generally low back-bonding abilities, that metal → aryl π delocalization could have substantial importance. A similar conclusion can be drawn for other ligands. For example, 2,2′-bipyridyl can stabilize many low-valent complexes presumably by virtue of π back-bonding ability,[81] yet this ligand seems to possess a vanishingly small back-bonding capacity in carbonyl complexes.[51]

Acknowledgment. We wish to thank Dr. L. C. Dickinson, Mrs. J. Newberry, Mr. A. Jones, and Mr. W. Goldberg for their assistance in obtaining the ^{19}F nmr spectra. We acknowledge the financial support for this work from the National Science Foundation through Grant GP-8140, and fellowship support to R. P. S. from the University of Wisconsin Graduate School from a grant from the National Aeronautics and Space Administration.

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[76] Recent esr studies on *trans*-$(p\text{-}XC_6H_4)_2CoL_2$ complexes (L = $P(C_2H_5)_2C_6H_5$) support this contention; see K. Matsuzaki and T. Yasukawa, *Chem. Commun.*, 1460 (1968).

[77] Metal–*aryl* carbon bond lengths are known for a variety of transition metal–aryl complexes,[18–27] but to date none of the corresponding metal–*alkyl* carbon distances have been determined. Instead the latter distances must be estimated from the appropriate metal–carbon covalent radii sum. Although the covalent radii of sp^3 and sp^2 hybridized carbon are well established and roughly constant, metallic radii are influenced by (a) the effective charge on the metal nucleus, (b) the metal coordination number, (c) the coordination geometry, and (d) the electronic and steric requirements imposed by other ligands bonded to the metal.[78–80] Until the corresponding metal–alkyl and metal–aryl distances are obtained in *completely analogous* complexes, the present crystallographic evidence for a strong contribution to the metal–aryl bond must be considered inconclusive.

[78] L. F. Dahl, R. J. Doedens, W. Hübel, and J. Nielsen, *J. Amer. Chem. Soc.*, **88**, 446 (1966).

[79] P. W. Sutton and L. F. Dahl, *ibid.*, **89**, 261 (1967).

[80] D. L. Stevenson and L. F. Dahl, *ibid.*, **89**, 3721 (1967).

[81] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, pp 755–756.

Nuclear Magnetic Resonance Investigation of Complexes Formed by Arsenic Pentafluoride and Some Very Weak Bases

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Abstract: The ^{19}F nmr spectra of the following systems have been studied over a range of temperature: AsF_5–SO_2F_2, AsF_5–SOF_2–SO_2F_2, AsF_5–SO_2FCl, AsF_5–SO_2–SO_2F_2, AsF_5–CH_3SO_2F–SO_2F_2, and AsF_5–CH_3SO_2F–SO_2F_2–SO_2. It has been found that AsF_5 forms very labile complexes with SOF_2, SO_2, SO_2FCl, and CH_3SO_2F, but no complex formation was observed with SO_2F_2.

It has been shown recently that antimony pentafluoride forms complexes with the very weak bases SO_2FCl, SOF_2, SO_2, and CH_3SO_2F.[1] Although evidence has been obtained for stable complexes of arsenic pentafluoride with relatively strong bases such as CH_3CN,[2] $(CH_3)_3N$, and $(CH_3)_2O$,[3] except for a study of the AsF_5–SO_2 system,[4] in which it was concluded that no adduct formation occurred, there has been no investigation of the possibility of adduct formation with very weak bases. We have used ^{1}H and ^{19}F nmr to investigate the interaction of AsF_5 with SO_2F_2, SOF_2, SO_2FCl, SO_2, and CH_3SO_2F.

Results and Discussion

The AsF_5–SO_2F_2 System. No complex formation occurs between AsF_5 and SO_2F_2 even at −140°. The ^{19}F spectra of a 1:4.25 AsF_5:SO_2F_2 sample showed only a single F-on-S peak with the same chemical shift as that found for pure SO_2F_2. The F-on-As peak was very broad (more than 1000 Hz at −35°) as for pure AsF_5, and in contrast to our findings for AsF_5 with stronger donors which form complexes. This result is not surprising as SO_2F_2 does not form any complex with SbF_5.[1] In fact in solution in SO_2F_2, SbF_5 forms fluorine-bridged chains as in liquid SbF_5, rather than complex with SO_2F_2. It is known from vibrational spectroscopy that AsF_5 is monomeric in the liquid as well as the gas phase[5] so that in this case the formation of polymeric fluorine bridged chains does not compete with the formation of an $AsF_5 \cdot SO_2F_2$ complex. Since no interaction occurs, SO_2F_2 was used as a solvent for the other potential bases that were studied in order to obtain the nmr spectra at temperatures down to the freezing point of SO_2F_2 (−135.8°).[6]

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[1] P. A. W. Dean and R. J. Gillespie, *J. Amer. Chem. Soc.*, **91**, 7260 (1969).

[2] F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, **6**, 129 (1967).

[3] L. Lunazzi and S. Brownstein, *J. Magn. Resonance*, **1**, 119 (1969).

[4] E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *Chem. Ind.* (London), 117 (1951).

[5] L. C. Hoskins and R. C. Lord, *J. Chem. Phys.*, **46**, 2402 (1967).

[6] F. J. Bockhoff, R. V. Petrella, and E. L. Pace, *ibid.*, **32**, 799 (1960).