COMMUNICATION

EFFECT OF A SERIES OF PHOSPHINE AND PHOSPHITE LIGANDS ON THE TAFT SUBSTITUENT CONSTANTS OF ARENECHROMIUMCARBONYL AND CYCLOPENTADIENYLMANGANESECARBONYL COMPLEXES

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Abstract—A series of m- and p-fluorophenylarenechromiumcarbonyl and m- and p-fluorophenylcyclopentadienylmanganesecarbonyl complexes of phosphines and phosphites have been prepared and characterized by IR and NMR spectroscopy. Taft substituent constants were calculated from the ¹⁹F chemical shifts and carbonyl stretching force constants were calculated from the carbonyl stretching frequencies of the compounds. It has been found that the phosphine and phosphite groups exert parallel effects on the Taft constants and stretching force constants and, furthermore, that the trends in the chromium and manganese series are strongly related.

The physical and chemical properties of organometallic compounds are known to be sensitive to the nature of the ligands bound to the metal atom. For example, variations of carbonyl stretching frequencies of metal carbonyl complexes of the type $LM(CO)_n$ were used to establish the order of π acidities for a broad series of phosphine and phosphite ligands.¹ Similarly, Bodner *et al.*² have related the carbonyl ¹³C NMR chemical shifts of a variety of $LM(CO)_n$ complexes to the σ and π acidity of the ligands. Work in this laboratory on dihydrogen evolution from dinuclear organometallic complexes has demonstrated that the rates of these reactions are affected by the electron donor properties of phosphine groups bound to the metal atom.³

As much of our research concerns the manipulation of the electron density, or basicity, at a reactive metal atom, we have sought methods which can provide a quantitative measure of the electronic changes brought about by varying the ligands on a metal atom. One technique which is well suited to organometallic chemistry is the measurement of Taft substituent constants by examination of the ¹⁹F NMR chemical shifts of substituted *m*- and *p*fluorobenzenes.⁴ This technique is broadly applicable to organometallic compounds, including those which are too air or water sensitive to survive other methods. Parshall has reported Taft substituent constants for a series of σ -bonded aryl compounds of Ni, Pd and Pt.⁵ Stewart and Treichel have examined a large number of σ -bonded complexes of metal carbonyls and mixed carbonyl, phosphine compounds as well as cyclopentadienyl compounds.⁶ Nesmeyanov et al. have reported substituent constants for σ -bonded aryl derivatives of cyclopentadienylmetalcarbonyl compounds, where the metals were iron, molybdenum and tungsten.⁷ These workers also reported the substituent constants for cyclopentadienyliron metallated arene rings.⁸ Gubin et al. have been concerned with the effect of metallation on the cyclopentadienyl ring and have reported substituent constants for the iron group metallocenes,9 cymantrene and its rhenium analog,¹⁰ and for alkali metal complexed cyclopentadienide anions.¹¹ This group also reported substituent constants for the arenechromiumtricarbonyl moiety.¹²

We have reported the Taft substituents of a set of $[(\text{arene})Cr(CO)_2L]$ complexes (where L = CO, PPh₃ and AsPh₃).¹³ It was shown that both the inductive, σ_I and resonance, σ_R^0 , substituent constants of the metallated arene are sensitive to the identity of L.

In order to gain a better understanding of the relationship between the Taft constants and the metal ligands, we have prepared an extended series of m- and [(p-fluorophenylarene)Cr(CO)₂L] (I) and CpMn(CO)₂L (II) complexes and determined the Taft substituent constants of these compounds.



As an expansion of these studies, we have calculated the stretching force constants of these compounds using the approximations developed by Cotton and Kraihanzel.¹⁴ Linear regression analysis has been used to examine the correlations between stretching force constants and Taft constants within and between the sets of compounds.

RESULTS AND DISCUSSION

m- and *p*-Fluorobiphenylchromiumtricarbonyl can be prepared in good yield by reaction of the appropriate biphenyl with chromium hexacarbonyl in refluxing butyl ether–THF according to the procedures of Top and Jaouen.¹⁵ Photolysis of these complexes in benzene in the presence of phosphines or phosphites gives the corresponding [(arene) $Cr(CO)_2L$] complexes in good yield.¹⁶

Substituted CpMn(CO)₃ derivatives were prepared by reaction of *m*- or *p*-fluorophenylcyclopentadienylthallium with BrMn(CO)₅. Gubin *et al.* have prepared these compounds from the analogous cyclopentadienyl sodium salts.¹⁰ As in the chromium series, photolysis of the manganese carbonyl compounds in benzene gave the phosphine and phosphite complexes in good yield.¹⁷

Analyses and physical data on the new compounds are presented in Table 1. In several cases it was not possible to obtain elemental analyses because of the instability of the complexes. For those materials the spectral data were taken to be sufficient proof of identity.

Spectra of all compounds were recorded in deuterobenzene. In the cases of the trimethylphosphine derivatives of manganese the air-sensitivity of the compounds precluded rigorous purification, so ¹H NMR spectra were not recorded. ¹⁹F NMR chemical shifts were measured relative to both C_6F_6 and C_6H_5F to insure reproducibility. ¹⁹F chemical shifts are reported relative to C_6F_6 . ³¹P NMR chemical shifts were measured relative to 85% H_3PO_4 . The

Compound					
$[(Arene)Cr(CO)_2L]$	The	eory	For	und	
L (<i>m</i> / <i>p</i> -F)	%C	%H	%C	%Н	M.p.
$P(OCH_2CF_3)_3 (m-F)$		_			Yellow-orange oil
$P(OCH_2CF_3)_3(p-F)$		_			Yellow-orange oil
$P(OC_6H_5)_3 (m-F)$	65.1	4.1	64.8	4.2	112–114°C
$P(OC_6H_5)_3(p-F)$	65.1	4.1	65.2	4.3	128–130°C
$P(OCH_3)_3 (m-F)$	50.5	4.5	50.5	4.4	96.98°C
$P(OCH_3)_3 (p-F)$	50.5	4.5	50.4	4.5	121–123°C
$P(CH_3)_3 (m-F)$	57.3	5.1	55.4	5.2	42–43°C
$P(CH_3)_3 (p-F)$	57.3	5.1	57.0	5.1	Yellow oil
$P(C_4H_9)_3$ (m-F)		_			Orange oil
$P(C_4H_9)_3(p-F)$					Orange oil
CpMn(CO) ₂ L L (m/p-F)					
$P(OC_6H_5)_3 (m-F)$	64.1	4.0	64.2	4.4	99–100°C
$P(OC_6H_5)_3(p-F)$	64.1	4.0	63.6	4.2	115–117°C
$P(C_6H_5)_3 (m-F)$	69.9	4.3	71.2	4.6	96–97°C
$P(C_6H_5)_3(p-F)$	69.9	4.3	69.6	4.3	111–112°C
$P(CH_3)_3 (m-F)$	_	_			Yellow oil
$P(CH_3)_3 (p-F)$				takan series	Yellow oil

Table 1. Analytical data and physical properties of new compounds

phosphorus resonances of the chromium compounds were all sharp singlets, while those of the manganese series were broadened. Presumably coupling between the phosphorus and the 5/2 spin manganese atom is responsible for the broadening. All NMR spectral parameters are presented in Table 2.

IR spectra of all compounds were recorded in chloroform and the carbonyl stretching frequencies are presented in Table 3. Force constants for the chromium and manganese series were calculated by use of the approximations developed by Cotton and Kraihanzel and are also presented in Table 3.

The Taft substituent constants were computed using the relationships developed by Taft *et al.*⁴ and are presented in Table 4. In principle, the σ_I value is a relative measure of the ability of a substituent to inductively contribute or withdraw electron density from the fluorophenyl ring, while the σ_R^0 is a measure of the resonance contributions from the substituent.

Linear regression analysis was used to determine correlations between selected sets of data and the slopes, intercepts and correlation coefficients for these sets of data are presented in Table 5. Several broad observations can be made on the basis of these correlations. (1) In general, the correlation between stretching force constants and σ_R^0 are better than those between the force constants and σ_I substituent constants. (2) There is a good correlation between σ_R^0 and σ_I within a metal series. It is interesting that these sets of data seem to fall on the same line indicating that the relationship between inductive and resonance contributions are the same for the two series despite the fact that two different metals and quite different aromatic rings are being compared. (3) This last observation is reinforced by comparison of the σ_I and σ_R^0 constants between the two series for which the correlations are excellent.

These data indicate that electron density at the metal atoms increases in the order:

$$P(OCH_2CF_3)_3 \approx CO < P(OPh)_3 < P(OMe)_3$$
$$< AsPh_3 \approx PPh_3 < PMe_3 \approx PBu_3$$

Parallel trends have been reported by Tolman¹ for carbonyl stretching frequencies and by Bodner *et al.*² for ¹³C chemical shifts of carbonyl carbons.

Of particular interest is the similarity between $P(OCH_2CF_3)_3$ and CO. Shreeve and Williamson have recently reported the first synthesis of metal complexes containing this interesting, strongly electron withdrawing ligand.¹⁸ As no complete multinuclear NMR analysis of this compound has previously been reported, we have included the ¹H, ¹⁹F and ³¹P NMR chemical shift and coupling constants in Table 2. Spectral data presented by Shreeve and Williamson and our own observations indicate that the spin-spin coupling between the phosphorus atom and the fluorine atoms is damped by complexation to metals.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer Model 1750 FT/IR Spectrophotometer. NMR spectra were recorded on a Varian Associates FT80A NMR Spectrometer. Thallium ethoxide,¹⁹ cyclopentenone²⁰ and *m*- and *p*-fluorobiphenyl²¹ were prepared by literature procedures. Chromium hexacarbonyl and bromomanganesepentacarbonyl were purchased from Strem, and *m*- and *p*-bromofluorobenzene were purchased from Aldrich. Purchased materials were used as received. Photolysis reactions were conducted in dry, air-free benzene which was distilled from sodium under N₂ immediately before use. Photolyses were conducted in an Ace doubly-jacketed photolysis vessel with a quartz inner vessel using a medium pressure mercury lamp. Phosphine and phosphite derivatives of arenechromiumtricarbonyl and cyclopentadienylmanganesecarbonyl complexes were prepared by photochemical exchange of phosphine for carbonyl in benzene solution as has been previously reported.¹³ Microanalysis was conducted by Micro-Analysis Inc. of Wilmington, DE.

Synthesis of m- and p-fluorophenylcyclopentadiene

Cyclopentenone (10.0 g, 0.12 mol), was placed in a 250 cm³ three neck flask outfitted with an addition funnel, reflux condenser and nitrogen inlet. About 100 cm³ of ethyl ether was added to the flask and the contents were cooled to -5 to -10° C in a salt-ice bath.

m-Fluorophenylmagnesiumbromide in ethyl ether (prepared from *m*-bromofluorobenzene (20.8 g, 0.12 mol), and 4.9 g of magnesium turnings over a 3 h period) was added over 90 min to the cyclopentenone solution. (Note: *m*- and *p*-bromofluorobenzenes are severe skin irritants and have been found to cause chloracne in this laboratory. They should both be handled with appropriate protective equipment.) A pink precipitate formed immediately. After addition was complete the suspension was stirred for an additional 90 min at -5° C.

The pink suspension was poured into 300 cm³ of ice-cold concentrated aqueous ammonia saturated with ammonium chloride in a 1 l separatory funnel and shaken vigorously. The organic layer separated and the aqueous layer was extracted with three, 100

1	19-1	310
'H	···F·	5- P
6.96 (4H, s) 4.92 (2H, m) 4.54 (3H, m) 3.97 (6H, m)	50.75 (F—Ph) 88.05 (t, J _{F—H} = 8.28 Hz)	215.13
7.15 (4H, m) 4.39–4.01 (5H, m) 3.92 (6H, m)	50.49 (F—Ph) 88.12 (t, $J_{F-H} = 8.01$ Hz)	212.40
7.16 (m) 4.55 (broad s)	50.08	185.62
7.15 (m) 4.54 (broad s)	49.42	185.57
7.16 (4H, m) 4.97 (2H, m) 4.66 (3H, m) 3.32 (9H, d, <i>J</i> _{P-H} = 11.1 Hz)	50.01	215.22
6.98 (4H, AB quartet) 4.94 (2H, m) 4.69 (3H, m) 3.34 (9H, d, J _{P-H} = 11.1 Hz)	48.83	215.63
7.00 (4H, m) 4.81 (2H, m) 4.40 (3H, m) 0.93 (9H, d, J _{P—H} = 7.3 Hz)	49.74	38.61
7.02 (4H, m) 4.78 (2H, m) 4.43 (3H, m) 0.95 (9H, d, J _{P-H} = 7.7 Hz)	48.05	39.08
7.30–6.90 (4H, m) 5.19 (2H, s) 4.89 (3H, s) 1.37 (18H, m) 0.87 (9H, m)	46.63	60.22
7.30–6.90 (4H, m) 5.13 (2H, s) 4.87 (3H, s) 1.37 (18H, m) 0.87 (9H, m)	48.87	60.75
7.33-6.78 (4H, m) 4.26 (2H, broad s) 3.88 (2H, broad s)	49.78	Not observed
7.26–6.76 (4H, m) 4.25 (2H, m) 3.94 (2H, m)	48.56	Not observed
7.50–6.97 (15H, s) 4.52 (2H, broad s) 4.02 (2H, broad s)	49.54	91.42
	¹ H 6.96 (4H, s) 4.92 (2H, m) 4.54 (3H, m) 3.97 (6H, m) 7.15 (4H, m) 4.39–4.01 (5H, m) 3.92 (6H, m) 7.16 (m) 4.55 (broad s) 7.16 (m) 4.54 (broad s) 7.16 (4H, m) 4.97 (2H, m) 4.66 (3H, m) 3.32 (9H, d, $J_{P-H} = 11.1$ Hz) 6.98 (4H, AB quartet) 4.94 (2H, m) 4.69 (3H, m) 3.34 (9H, d, $J_{P-H} = 11.1$ Hz) 7.00 (4H, m) 4.81 (2H, m) 4.40 (3H, m) 0.93 (9H, d, $J_{P-H} = 7.3$ Hz) 7.02 (4H, m) 4.43 (3H, m) 0.95 (9H, d, $J_{P-H} = 7.7$ Hz) 7.30–6.90 (4H, m) 5.19 (2H, s) 4.89 (3H, s) 1.37 (18H, m) 0.87 (9H, m) 7.30–6.90 (4H, m) 5.13 (2H, s) 4.87 (3H, s) 1.37 (18H, m) 0.87 (9H, m) 7.30–6.90 (4H, m) 5.13 (2H, s) 4.87 (3H, s) 1.37 (18H, m) 0.87 (9H, m) 7.30–6.97 (15H, s) 4.52 (2H, broad s) 3.88 (2H, broad s) 7.26–6.76 (4H, m) 4.25 (2H, m) 3.94 (2H, m) 7.50–6.97 (15H, s) 4.52 (2H, broad s) 4.02 (2H	1 H 19 F16.96 (4H, s)50.75 (FPh)4.92 (2H, m)88.05 (t, $J_{F-H} = 8.28$ Hz)4.54 (3H, m)50.49 (FPh)3.97 (6H, m)88.12 (t, $J_{F-H} = 8.01$ Hz)3.97 (6H, m)50.49 (FPh)4.39 -4.01 (SH, m)88.12 (t, $J_{F-H} = 8.01$ Hz)3.92 (6H, m)50.087.15 (m)49.424.54 (broad s)7.15 (m)7.15 (m)49.424.54 (broad s)7.16 (4H, m)7.16 (4H, m)50.014.97 (2H, m)48.834.66 (3H, m)3.32 (9H, d, $J_{P-H} = 11.1$ Hz)3.32 (9H, d, $J_{P-H} = 11.1$ Hz)7.00 (4H, m)3.34 (9H, d, $J_{P-H} = 7.3$ Hz)7.02 (4H, m)7.00 (4H, m)48.054.81 (2H, m)48.054.43 (3H, m)9.749.95 (9H, d, $J_{P-H} = 7.7$ Hz)7.30-6.90 (4H, m)46.635.19 (2H, s)48.874.87 (3H, s)1.37 (18H, m)0.87 (9H, m)48.877.33-6.78 (4H, m)48.763.88 (2H, broad s)7.26-6.76 (4H, m)3.88 (2H, broad s)3.88 (2H, broad s)3.88 (2H, broad s)3.89 (2H, m)3.84 (2H, m)48.564.25 (2H, m)3.94 (2H, m)3.94 (2H, m)48.564.25 (2H, m)3.94 (2H, m)3.94 (2H, m)49.54

Table 2. NMR spectral data for [(Arene)Cr(CO)₂L] and CpMn(CO)₂L complexes in C_6D_6

Table 2–	-continued		······
'Η		¹⁹ F ¹	³¹ P
7.51–6.98 (15H, s) 4.51 (2H, broad s) 4.04 (2H, broad s)	47.86		91.94
_	50.36		Not observed

47.35

87.60 (d of t)

 $J_{\text{F}--\text{H}} = 8.20 \text{ Hz}$

 $J_{P-F} = 4.60 \text{ Hz}$

Table 2-continued

 C_6H_5F is 49.98 ppm relative to C_6F_6 .

3.56 (d of t)

 $J_{\rm F-H} = 8.20 \; {\rm Hz}$

 $J_{P-H} = 8.14 \text{ Hz}$

Compound CpMn(CO)₂L L (m/p-F)

 $P(C_6H_5)_3(p-F)$

P(CH₃)₃ (m-F)

P(CH₃)₃ (*p*-F)

P(OCH₂CF₃)₃

101	~ consur	11.5	
Compound [(Arene)Cr(CO) ₂ L] L (m/p-F)	CO Sym	k(CO) (10 ⁵ dyn cm ⁻¹)	
	•		· · · · · · · · · · · · · · · · · · ·
CO (<i>m</i> -F)	1978	1902	15.00
CO (<i>p</i> -F)	1980	1900	15.02
$P(OCH_2CF_3)_3 (m-F)$	1920	1860	14.46
$P(OCH_2CF_3)_3(p-F)$	1921	1863	14.43
$P(OPh)_3 (m-F)$	1917	1860	14.40
$P(OPh)_3(p-F)$	1918	1860	14.41
$P(OMe)_3 (m-F)$	1903	1846	14.20
$P(OMe)_3(p-F)$	1903	1844	14.18
$AsPh_3(m-F)$	1902	1850	14.22
$AsPh_3(p-F)$	1897	1837	14.08
$PPh_3(m-F)$	1895	1837	14.06
$PPh_3(p-F)$	1890	1836	14.02
$PMe_1(m-F)$	1888	1828	13.94
$PMe_{3}(p-F)$	1885	1828	13.92
$PBu_{3}(m-F)$	1883	1835	13.96
$PBu_3(p-F)$	1885	1826	13.91
CpMn(CO) ₂ L L (<i>m</i> / <i>p</i> -F)			
CO (<i>m</i> -F)	2010	1926	15.43
CO (<i>p</i> -F)	2010	1930	15.47
$P(OPh)_3 (m-F)$	1960	1895	15.01
$P(OPh)_3(p-F)$	1960	1895	15.01
$PPh_3(m-F)$	1930	1865	14.52
$PPh_3(p-F)$	1933	1862	14.54
$PMe_3(m-F)$	1938	1860	14.57
$PMe_3(p-F)$	1924	1852	14.40

Table 3.	Carbonyl	stetching	frequencies	and	stretching
		force con	nstants		

cm³ portions of ethyl ether. The combined ether extracts were dried over magnesium sulphate. After removal of ethyl ether by rotary evaporator, the remaining yellow oil was distilled under high vacuum to give a mixture of *m*-fluorophenylcyclopentadiene isomers. The portion between 160– 210°C was recovered. The fluorophenylcyclopentadiene prepared in this way was used immediately without further purification.

Table 4. Taft substituent constants for $[(Arene)Cr(CO)_2L]$ and $CpMn(CO)_2L$

σ_I	$-\sigma_R^0$
0.173	0.004
0.193	0.009
0.099	0.022
0.089	0.043
0.065	0.047
0.062	0.042
0.051	0.057
0.037	0.057
0.141	0.024
0.056	0.041
0.023	0.057
0.014	0.072
	σ ₁ 0.173 0.193 0.099 0.089 0.065 0.062 0.051 0.037 0.141 0.056 0.023 0.014

45.60 (broad)

 $J_{\rm F-P} = 4.60 \text{ Hz}$

138.30 (m)

				The second s
x	у	m	b	r
k(CO) (Cr)	$\sigma_I(Cr)$	0.135	-1.834	0.845
k(CO) (Cr)	σ_R^0 (Cr)	0.0532	-0.795	0.916
k(CO) (Mn)	$\sigma_I(Mn)$	0.125	-1.823	0.855
k(CO) (Mn)	$\sigma_R^{\rm o}$ (Mn)	0.0489	-0.781	0.934
k(CO) (Cr)	k(CO) (Mn)	0.707	4.843	0.870
$\sigma_I(Cr)$	σ_R^0 (Cr)	0.344	-0.0681	0.947
$\sigma_I(Mn)$	σ_R^0 (Mn)	0.333	-0.0680	0.934
$\sigma_I(Cr)$	$\sigma_I(Mn)$	1.048	-0.0423	0.998
σ_R^0 (Cr)	σ_R^0 (Mn)	0.892	-0.0206	0.999
σ_I (all)	σ_R^0 (all)	0.342	-0.0682	0.949

Table 5. Linear regression analysis of $[(Arene)Cr(CO)_2L]$ and $CpMn(CO)_2L$ spectral data^{*a*}

^{*a*} Data are presented for the relationship : y = mx + b.

Linear regression calculations were performed using standard statistical methods. The correlation coefficient R is reflective of "goodness of fit" where R = 1.0 for a perfect straight line.

p-Fluorophenylcyclopentadiene can be prepared similarly. Typical yields are 50–80%.

Synthesis of thallium m- and p-fluorophenylcyclopentadienide

m- or *p*-Fluorophenylcyclopentadiene (8.5 g, 22 mmol), were taken up in 100 cm³ of ethanol in a 250 cm³ round bottom flask. A septum was fitted onto the flask and the contents were flushed with nitrogen using a syringe for 5 min. Thallium ethoxide (7.0 g, 29 mmol), was added slowly by syringe to give a yellow precipitate which formed immediately. After all of the thallium ethoxide had been added, the suspension was allowed to stir for 1 h and then filtered on a medium glass frit funnel. The yellow solid was washed once with 10 cm³ of ethanol, 10 cm³ of ethyl ether and then with hexane. Yield : 80–90%.

Thallium cyclopentadienyl compounds are stable in air for short periods but darken on long exposure to air or light. They should be stored under nitrogen in the cold. Under these conditions they are stable for several months. (Note: Thallium compounds are highly toxic and should be handled with gloves.)

Synthesis of m- and p-fluorophenylcymantrene

Thallium fluorophenylcyclopentadienide (5.0 g, 14 mmol), were placed in a 250 cm³ round bottom flask and the flask was flushed with nitrogen. About 100 ml of dry, air-free benzene was added to the flask followed by bromomanganesepentacarbonyl (3.8 g, 14 mmol). The reaction flask was outfitted

with a reflux condenser and the mixture was refluxed overnight. The reaction mixture was filtered hot through Celite and the solvent removed by rotary evaporator. The resulting orange-yellow solid was chromatographed on alumina using 10% methylene chloride in petroleum ether as an eluant. *m*- and *p*-Fluorophenylcymantrene were recovered as orange-yellow crystalline solids after solvent removal.

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