THE PREPARATION AND PROPERTIES OF TRIFERROCENYLPHOSPHINE DERIVATIVES OF METAL CARBONYLS

CHARLES U. PITTMAN, JR. and GEORGE O. EVANS*

Department of Chemistry, The University of Alabama, University, Alabama 35486 (U.S.A.)

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SUMMARY

The triferrocenylphosphine monosubstitution products of $M(CO)_6$ (M = Cr, Mo, W), $Fe(CO)_5$ and $Mn_2(CO)_{10}$ have been prepared and characterized. The CO stretching spectra have been compared with those of the triphenylphosphine analogs. Simplified sets of force constants describing the CO stretching vibrations have been computed for the Group VI derivatives according to the method of Cotton and Kraihanzel, and from these the σ-donor and π-acceptor properties of the ligand evaluated. Triferrocenylphosphine is a better donor ligand than triphenylphosphine.

INTRODUCTION

In 1965 the synthesis of the unusual molecule, triferrocenylphosphine, P-$(C_5H_4FeC_5H_5)_3$ (hereafter abbreviated TFP) was reported by Sollot and Peterson[1]. Its properties as a coordinating ligand had, to the best of our knowledge, gone wholly unnoticed until very recently, when Nesmeyanov and coworkers[2] reported the photochemical preparation of the monosubstituted TFP derivatives of π-$C_5H_5Mn(CO)_3$ and π-$C_6H_6Cr(CO)_3$.

It was of interest to compare the thermal reactivity of this very bulky tertiary phosphine with other known ligands in the presence of various metal carbonyls. In addition, it was of interest to evaluate the σ-donor and π-acceptor properties of TFP when coordinated to the metal species. The method of Graham[3], where these synergic bonding effects have been semi-quantitatively correlated for a large number of ligands with the axial and equatorial CO stretching constants of the pseudo-octahedral molybdenum pentacarbonyl derivatives, appeared to be the method of choice for dissecting the σ-donor and π-acceptor abilities of TFP. Furthermore, in view of the recent studies of the semiconductivity of biferrocene[3] and several ferrocenyl-containing polymers[5] upon partial oxidation, the oxidative properties of TFP derivatives are of future interest. With these thoughts in mind we synthesized, characterized, and now report the complexes, $M(CO)_5TFP$ (M = Cr, Mo, W), $Fe(CO)_4TFP$ and Mn_2-$(CO)_9TFP$.

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* Air Force Postdoctoral Fellow 1971–1972, to whom inquiries should be sent.

EXPERIMENTAL

The yellow powdery TFP utilized in this study was prepared by a modification of Sollot's method[1] and characterized by its melting point (m.p. 270–271°; lit.[1] 271–273°), PMR spectroscopy (Table 1, footnote *a*), and mass spectrometry (parent ion observed). Metal carbonyls were purchased from Pressure Chemical and used without further purification. Diglyme was used directly from a fresh bottle. Solution IR spectra of all metal carbonyl derivatives of TFP were measured in the CO stretching region

TABLE 1

PHYSICAL PROPERTIES[a], YIELDS, AND ANALYSES FOR THE COMPOUNDS $M(CO)_5TFP$ (M=Cr, Mo, W), $Fe(CO)_4TFP$ AND $Mn_2(CO)_9TFP$.

Compound	Color	M.p. (°C)	Yield (%)	Analyses		$\nu(CO)^b$ (cm^{-1})	Visible (Å)
				Found	Calcd.		
$Cr(CO)_5TFP$	Orange	185–193 gradual decomposition	82	C 54.02	54.41	2058 m	4590
				H 3.49	3.82	1977 w	
				O 10.28	9.98	1935 s(br)	
				Fe 21.53	21.00		
				P 3.98	4.09		
				Cr 6.68	6.66		
$Mo(CO)_5TFP$	Orange	190–195 gradual decomposition	84	C 51.13	50.91	2068 m	4490
				H 3.31	3.30	1982 w	
				O 9.73	9.88	1943 s(br)	
				Fe 20.38	19.27		
				P 3.76	3.77		
				Mo 11.67	11.60		
$W(CO)_5TFP$	Orange	210–217 gradual decomposition	78	C 46.19	46.30	2067 m	4530
				H 2.99	2.95	1974 w	
				O 8.79	8.79	1934 s(br)	
				Fe 18.41	18.30		
				P 3.40	3.49		
				W 20.20	20.03		
$Fe(CO)_4TFP$	Orange	225–230 gradual decomposition	23	C 54.16	53.81	2047 m^c	4500
				H 3.61	3.52	1969 m	
				O 8.48	8.67	1938 s (doublet)	
				Fe 29.62	29.43	1929	
				P 4.10	4.17		
$Mn_2(CO)_9TFP$	Red-orange	235–240 gradual decomposition	52			2090 m^d	
						2005 w–m	
						1991 s	
						1956 m(br)	
						1931 m(br)	

[a] PMR spectrum of $Cr(CO)_5TFP$ (τ=4.93 m, 4.91 m, 5.36 s; $CDCl_3$). PMR spectrum of TFP (τ=5.16 m, 5.26 m, 5.39 s; $CDCl_3$ solution, TMS reference (m=multiplet). [b] $CHCl_3$ solution. [c] $Fe(CO)_4PPh_3$ [$\nu(CO)$: 2059(3), 1978(3), 1938(10); $CHCl_3$ solution][11]. [d] $Mn_2(CO)_9PPh_3$[$\nu(CO)$: 2093 m, 2011 m, 1994 vs, 1973 m, 1939 m; hexane solution][12]. [e] $CHCl_3$ solution. TFP [4430 Å; $CHCl_3$ solution].

(1800–2200 cm^{-1}) in CHCl$_3$ on a Beckman IR-7 spectrometer (± 1 cm^{-1}) and are recorded in Table 1. The PMR spectrum of both Cr(CO)$_5$TFP and TFP were recorded on the Varian HA-100 instrument using a saturated CDCl$_3$ solution (TMS as internal standard) and are listed in footnote a of Table 1.

The mass spectrum of Cr(CO)$_5$TFP was recorded on a CEC 21-104 instrument at 70 eV. However, no ions with m/e greater than 586 (TFP$^+$) could be observed. No attempt was made to observe parent ions for the other derivatives.

Peak positions for the weak absorptions ($^1A_{1g} \rightarrow a^1E_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{2g}$) characteristic of the ferrocenyl group[6] were measured on a Cary 14 spectrophotometer using CHCl$_3$ solutions of the Group VI and iron derivatives in 1 cm matched cells (Table 1). The peak position obtained for the ligand itself is recorded in footnote e (Table 1).

Simplified sets of three force constants yielding a best least squares fit of the four CO stretching frequencies were computed for each of the Group VI derivatives (Table 2) according to the scheme outlined by Cotton and Kraihanzel[7]. The least-squares fitting program, FPERT, developed by Schachtschneider[8] was employed on the Univac 1108 computer (University of Alabama).

The TFP monosubstituted derivatives of the Group VI hexacarbonyls were prepared in a manner similar to that reported for their triphenylphosphine analogs[9,10]. Reaction times used, however, appeared to be somewhat shorter: Cr(CO)$_6$ (1½ h), Mo(CO)$_6$ (1 h) and W(CO)$_6$ (1 h). The derivative of Fe(CO)$_5$ was prepared in a manner similar to that used by Cotton in the synthesis of Fe(CO)$_4$PPh$_3$[11]. Mn$_2$(CO)$_9$TFP was also prepared thermally although the corresponding PPh$_3$ derivative had previously been synthesized photochemically[12].

In all cases the metal carbonyl was used in large excess in order to circumvent separation problems caused by the presence of unreacted TFP. Microanalyses of all

TABLE 2

COMPARISON OF CO STRETCHING FREQUENCIES^a, FORCE CONSTANTS^b, AND GRAHAM $\Delta\sigma$, $\Delta\pi$ PARAMETERS^c FOR THE MOLECULES M(CO)$_5$L (M=Cr, Mo, and W; L=TFP and PPh$_3$)

		Cr(CO)$_5$TFP		Cr(CO)$_5$PPh$_3$[7]	Mo(CO)$_5$TFP		Mo(CO)$_5$PPh$_3$[7]	W(CO)$_5$TFP		W(CO)$_5$PPh$_3$[7]
		Found	Calcd.		Found	Calcd.		Found	Calcd.	
(CO)	A_1^2	2058	2058.8	2070	2068	2068.1	2078	2067	2066.9	2074
	B_1	1977	1974.4	1984	1982	1982.1	1990	1974	1974.5	1981
	E	1935	1937.0	1944	1943	1943.3	1951	1934	1933.6	1943
	A_1^1		1934.9			1943.0			1934.0	
K_1		15.31±0.06		15.50	15.44±0.009		15.57	15.32±0.012		15.58
K_2		15.74±0.03		15.88	15.85±0.005		15.99	15.74±0.007		15.85
K_i		0.30±0.01		0.33	0.30±0.002		0.31	0.32±0.002		0.30
$\Delta\sigma$		−0.78		−0.69	−0.75		−0.60	−0.67		−0.71
$\Delta\pi$		0.75		0.80	0.77		0.76	0.67		0.82

All values measured on CHCl$_3$ solutions. ^{b} mdynes/Å. ^{c} Calculated using cyclohexylamine–M(CO)$_5$ as a reference [Cr(CO)$_5$Cy: $K_1 = 14.59$, $K_2 = 15.77$; Mo(CO)$_5$Cy: $K_1 = 14.65$, $K_2 = 15.83$; W(CO)$_5$Cy: $K_1 = 14.65$, $K_2 = 15.74$][15].

derivatives were performed by Meade Microanalytical Laboratory (Amherst, Mass.) and are presented in Table 1.

Preparation of Cr(CO)₅TFP, Mo(CO)₅TFP· and W(CO)₅TFP

Cr(CO)₆ (0.40 g; 1.8 mmol) and TFP (0.10 g; 0.17 mmol) were added to 25 ml of diglyme in a 50 ml flask equipped with a reflux condenser. After flushing with N₂, the solution was heated to reflux while maintaining a positive N₂ pressure. The sublimed carbonyl was manually returned to the reaction flask periodically. The color of the original deep orange solution faded to a light yellow over a period of 1.5 h. After cooling to room temperature, the solution was filtered in air and the solvent stripped under high vacuum (50–60°). The yellowish oily residues were dissolved in a minimal amount of CHCl₃, filtered, and petroleum ether (b.p. 30–60°) added to precipitate the powdery yellow product. Large well-formed crystals were easily grown by adding a small amount of toluene to a concentrated CHCl₃ solution of the product and slowly evaporating the CHCl₃ under a stream of N₂. The dark orange crystals were dried under vacuum and found to be analytically pure.

The preparations of W(CO)₅TFP and Mo(CO)₅TFP were identical except that Mo(CO)₅TFP was prepared at 135–145°.

Preparation of Fe(CO)₄TFP

TFP (0.15 g; 0.26 mmol) and Fe(CO)₅ (0.50 ml; 3.8 mmol) along with 4.0 ml of diglyme were introduced into a Fisher–Porter aerosol tube. The system was evacuated during three freeze–thaw cycles and heated in an oil bath at 125° for 6 h. During this period the solution became a deeper orange and within 3 h pillar-shaped orange crystals began forming on the walls of the tube. After cooling to room temperature and removing unreacted Fe(CO)₅ under vacuum, the solution was filtered and washed well with petroleum ether. The orange crystalline product was manually separated from any solid decomposition products, and after drying under vacuum, submitted for analysis.

Preparation of Mn₂(CO)₉TFP

Mn₂(CO)₁₀ (0.6 g; 1.5 mmol) and TFP (0.10 g; 0.17 mmol) were introduced into a Fisher–Porter tube along with 5 ml/of diglyme. Following evacuation of the tube at room temperature, it was heated to 125° for 17 h resulting in the formation of a bright orange solution. The reaction mixture was then chilled at −10° for 24 h resulting in the crystallization of excess Mn₂(CO)₁₀ along with the reddish-orange product. The mixture was filtered in air and the solid repeatedly washed with excess petroleum ether until the washings contained no more unreacted Mn₂(CO)₁₀. A small sample of the larger Mn₂(CO)₉TFP crystals was manually separated, dried under vacuum, and submitted for analysis.

DISCUSSION

Metallocenyl groups are generally considered to be electron-donating. Not only does ferrocene undergo facile electrophilic substitution reactions, but α-ferrocenyl carbonium ions are far more stable than their phenyl counterparts[6a]. Furthermore, the ruthenium portion of ruthenocenylferrocenylmethane undergoes a rever-
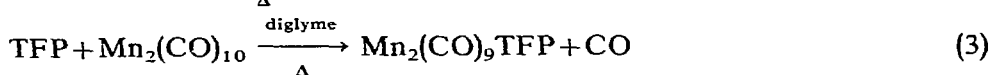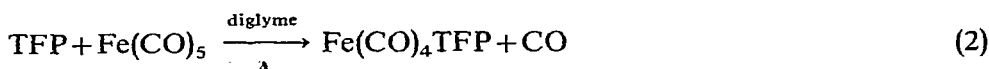
sible one-electron oxidation at a potential slightly lower than ruthenocene itself[13], suggesting that the unoxidized ferrocenyl ring system, as a donor, has enhanced the stability of the ruthenicenium nucleus. Because of this electron-releasing tendency, it was of interest to compare the donor characteristics of the very bulky TFP ligand with other tertiary phosphines while being aware of the fact that steric hindrance might preclude the formation of the metal carbonyl derivatives.

The monosubstitution products of the Group VI hexacarbonyls were easily prepared according to eqn. 1. The resulting orange crystalline derivatives were stable

$$(M = Cr, Mo, W)$$
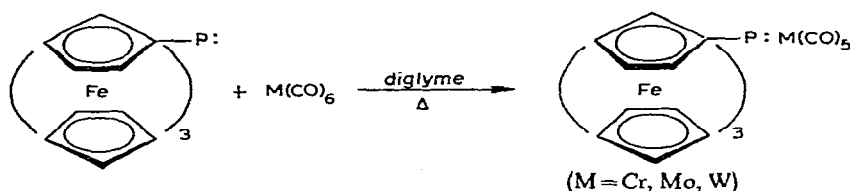
indefinitely in air and remained unchanged for extended periods (several days) in $CHCl_3$ solution under N_2. Although insoluble in alkanes, these compounds exhibit low to intermediate solubility in polar solvents while dissolving fairly well in $CHCl_3$. When the preparation of a disubstituted derivative of $Cr(CO)_6$ was attempted (TFP/carbonyl; 2/1 mole ratio) extensive decomposition was observed. This may suggest that steric compressions become serious when a second TFP ligand attempts to coordinate the metal, since other highly substituted phosphine derivatives have been made[14].

Both $Fe(CO)_4TFP$ and $Mn_2(CO)_9TFP$ were prepared thermally according to eqns. 2 and 3, respectively. Both compounds are stable in air but appear to be

$$TFP + Fe(CO)_5 \xrightarrow[\Delta]{diglyme} Fe(CO)_4TFP + CO \qquad (2)$$

$$TFP + Mn_2(CO)_{10} \xrightarrow[\Delta]{diglyme} Mn_2(CO)_9TFP + CO \qquad (3)$$

somewhat unstable in polar solvents under N_2. Furthermore, the manganese derivative decomposes readily in $CHCl_3$, presumedly due to the formation of chlorinated derivatives by means of a solvent induced cleavage of the metal–metal bond. Mn_2-$(CO)_{10}$ is known to behave in a similar fashion.

The donor character of TFP is suggested when one considers the visible absorption spectrum of the Group VI and iron TFP derivatives. Ferrocene, itself, exhibits a weak band at 440 nm which has been attributed to both $^1A_{1g} \rightarrow a^1E_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{2g}$ transitions[6b]. This band reportedly undergoes a bathochromic shift when electron-attracting groups are attached to the rings. Although there is a slight shift of this band to 443 nm in TFP, there occurs a much greater bathochromic shift of up to 19 nm upon coordination to the metal (Table 1) which results from the net flow of charge from the ligand to the metal carbonyl moiety.

The PMR spectrum of $Cr(CO)_5TFP$ exhibits a pair of broadened singlets, characteristic of the two sets of nonequivalent ring protons on the substituted ferrocenyl rings, and a sharp singlet arising from the protons on the unsubstituted rings at higher fields (Table 1). This sharp singlet is shifted very slightly downfield (0.03 ppm) from uncoordinated TFP (Table 1, footnote a). The pair of broadened singlets is

shifted to a greater extent indicative of electron withdrawal from these rings.

A cursory comparison of the CO stretching frequencies of the TFP-Group VI derivatives with those previously reported for the triphenylphosphine analogs[7] (Table 2) reveals that in all cases the former lie at correspondingly lower energies than the latter. This implies that more charge is being distributed into the CO antibonding orbitals in the case of the TFP substitution products. Similar shifts to lower energy are observed going from the PPh_3 to the TFP derivatives of the iron[11] and dimanganese carbonyls[12] (Table 1; see footnotes c and d). However, in comparing the dimanganese derivatives, this effect is not nearly so pronounced for several vibrational frequencies. These absorptions are presumedly due to those modes more nearly localized on the unsubstituted half of the binuclear molecule and hence are correspondingly more immune to substitutive effects. The spectral similarities of the TFP and PPh_3 derivatives suggests that TFP substitution has occurred axially for both molecules as previously established for the PPh_3 products[11,12].

The CO stretching frequencies of the Group VI derivatives may be easily assigned by analogy to corresponding PPh_3 derivatives[7] (Table 2). Although three IR active vibrations are theoretically expected for molecules of this type having C_{4v} symmetry $(2A_1 + E)$ it has previously been ascertained that the lower A_1 mode lies buried beneath the intense low energy E mode[7]. Consequently, the weak band of intermediate energy must be assigned to the B_1 mode (Raman active) which has gained some activity due to ligand-induced molecular distortion.

Using the assignments presented in Table 2, a simplified set of three force constants was computed for each of the Group VI derivatives according to the method of Cotton and Kraihanzel[7] (K_1 = axial CO stretching constant; K_2 = equatorial CO stretching constant; and K_i = cis interaction constant) giving a best fit of the observed spectrum. It is clear from Table 2 that excellent agreement was obtained between the calculated and observed frequencies for the molybdenum and tungsten derivatives. Although the fit for the chromium derivative is not nearly so attractive, it must be considered entirely satisfactory in view of the assumptions invoked in this method[7]. Comparison of the corresponding stretching constants, K_1 and K_2, computed for the respective TFP and PPh_3[7] derivatives (Table 2) reveals that in all cases the values for the TFP derivatives are significantly smaller. This emphasizes that greater localization of charge occurs in the CO antibonding orbitals of the TFP derivatives.

The σ-donor and π-acceptor components of this net ligand-to-metal charge flow were evaluated by computing the $\Delta\sigma$ and $\Delta\pi$ parameters of this ligand according to the method proposed by Graham[3]. These parameters were then compared with the values for the corresponding PPh_3 derivatives. Using the K_1 and K_2 values listed in Table 2, $\Delta\sigma$ and $\Delta\pi$ values were calculated for each species using as a reference the K_1 and K_2 values reported earlier for the cyclohexylamine Group VI pentacarbonyls[15]. All data used was obtained in $CHCl_3$ solutions. As seen in Table 2, these calculations suggest that TFP behaves as a significantly better donor than PPh_3 in the chromium and molybdenum derivatives (more negative $\Delta\sigma$ vlaues) whereas the π-backbonding capabilities of the two do not appear to differ greatly (more positive $\Delta\pi$ refers to greater backbonding character). However, it is quite surprising that, in the tungsten derivative, the σ-donor ability of PPh_3 appears to be greater than for TFP while at the same time the π-backbonding capability of TFP appears greatly diminished with respect to that of PPh_3. The combination of these two effects still gives rise to lower frequencies

for the TFP compound but seemingly for entirely different reasons than in the first two cases.

It is unclear just how much weight should be attached to these arguments due to the assumptions involved. However, there can be no doubt that TFP behaves as a very good ligand, and reactivity studies of its derivatives will surely form the basis of a number of interesting investigations. Not the least of these will be the progressive oxidation of the ferrocenyl nuclei (to ferricinium) using chemical agents such as dichlorodicyanoquinone[16]. The effect of such oxidation on the donor properties of phosphorus will be the subject of our future studies*.

ACKNOWLEDGEMENT

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* Upon completion of our studies a report of similar studies was made[17].