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Charge-transfer salts of carbonylmetalates as outer-sphere ion pairs in photochemical and thermal electron transfer *

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Abstract

Highly colored, crystalline salts result from the combination of the carbonylmetalates $Co(CO)_4^-$, $Mn(CO)_5^-$ and $HFe(CO)_4^-$ with perphenyl-phosphonium and sulfonium cations. The unique colors are associated with the interionic charge-transfer interactions of carbonylmetalates acting as electron donors and the onium cations as electron acceptors by the independent evaluation of their anodic and cathodic redox potentials E_p^a and E_p^c, respectively. Such charge-transfer salts exist as unperturbed contact ion pairs in the solid state and in solution, as is shown by their carbonyl (IR) spectra which establish the presence of $Co(CO)_4^-$, $Mn(CO)_5^-$ and $HFe(CO)_4^-$ in T_d, D_{3h} and C_{3v} symmetry of the undistorted anions. The rich photochemistry that accompanies the charge-transfer activation of these outer-sphere ion pairs is described and it is mechanistically placed in the context of photoinduced electron transfer followed by the facile reactions of phosphoranyl(sulfuranyl) and 17-electron carbonylmetal radical pairs. The analogous thermal annihilation of the iodonium salt $Ph_2I^+ Mn(CO)_5^-$ proceeds via an adiabatic electron transfer that is facilitated by an isoergonic driving force based on the enhanced reduction potential of Ph_2I^+.

Introduction

Organometallic anionic nucleophiles are frequently utilized as salts in conjunction with such large cations as PPN^+ (bis-triphenylphosphoranylideneammonium) and Ph_4P^+ (tetraphenylphosphonium) for their greater solubility, stability and crystallizability, since these cations are generally regarded as noninteracting and without significant ion-pairing consequences [1–3]. Indeed, X-ray crystallography has revealed the presence of Ph_4P^+ with undistorted tetrahedral symmetry in bromide and tribromide salts [4,5]. Nonetheless, as the formally phosphorous(V) derivative, Ph_4P^+ is the ultimate member of the homologous per-phenyl onium series, which includes such reactive cations as triphenylsulfonium (Ph_3S^+), diphenyliodonium (Ph_2I^+) and phenyldiazonium (PhN_2^+) whose active participa-

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* Dedicated to Professor A. Yamamoto on the occasion of his retirement.

tion in various nucleophile/electrophile reactions (both thermal and photochemical) is well known [6–9].

The electronic consequences of contact ion pairs (CIP) are often manifested by intermolecular charge-transfer absorption bands of the type originally described by Mulliken for electron donor–acceptor interactions [10–13]. Similarly, the structural consequences of "intimate" ion pairings have been detected in the infrared spectra of distorted ions, especially carbonylmetalate anions [14–16]. Accordingly, we have selected three representative organometallic anions, tetracarbonylcobaltate $Co(CO)_4^-$, pentacarbonylmanganate $Mn(CO)_5^-$, and hydridotetracarbonylferrate $HFe(CO)_4^-$, to prepare as the tetraphenylphosphonium and triphenylsulfonium salts for structural study. The deliberate actinic irradiation of these organometallic ion pairs also reveals the productive photochemistry that can derive from the activation of charge-transfer salts.

Results

Charge-transfer salts of carbonylmetalates

When colorless solutions of sodium tetracarbonylcobaltate and tetraphenylphosphonium chloride are mixed, bright yellow crystals separate spontaneously from the aqueous solution which remains singularly colorless. The colored salts of $Mn(CO)_5^-$ and $HFe(CO)_4^-$ with tetraphenylphosphonium also differ from those of their PPN^+ analogues, but more subtly — the pale yellow PPN^+ salts that contrast with the orange Ph_4P^+ salts. A similar appearance of color accompanies the mixing of colorless solutions of triphenylsulfonium hexafluorophosphate with the carbonylmetalates (*e.g.* $Ph_3S^+Mn(CO)_5^-$ is deep yellow).

Solvatochromism of charge-transfer salts

Dilute solutions (10^{-3} *M*) of the phosphonium salts in nonpolar organic solvents such as tetrahydrofuran ($D = 7.5$) or dichloromethane ($D = 9.1$) retain the characteristic colors of the crystalline salts [17]. However, the same salts dissolved in the polar acetonitrile ($D = 38$) yielded solutions which were colorless. The solvatochromism characteristic of these salts was quantitatively reflected in the electronic spectra of phosphonium solutions of carbonylmetalates. For example, the orange color of a THF solution of $Ph_3PCH_2Ph^+HFe(CO)_4^-$ arose from a broad unresolved visible absorption band which extended to beyond 500 nm (Fig. 1). In dichloromethane, which is slightly more polar [18], only the low-energy tail was observed owing to a significant blue shift of the absorption band. The further blue shift of the charge-transfer band in acetonitrile resulted in an essentially colorless solution of $Ph_3PCH_2Ph^+HFe(CO)_4^-$. Similarly the highly colored salts of $Ph_4P^+Co(CO)_4^-$, $Ph_4P^+Mn(CO)_5^-$ and $Ph_4P^+HFe(CO)_4^-$ in THF were characterized by significant visible absorptions that gradually weakened and blue-shifted as this solvent was changed to dichloromethane, then to acetonitrile.

The solvatochromism of the charge-transfer salts was quantitatively evaluated by comparing the spectral shift relative to a fixed absorbance in a standard solution of the salt [19,20]. Thus, Table 1 presents the CT wavelengths ($\lambda_{0.1}$) at which the various salt solutions (1.5×10^{-3} *M*) attained the arbitrary absorbance of 0.1 in three solvents. The blue shift of the CT band with increasing solvent polarity is apparent in Table 1 (left-to-right columns) by the monotonic decrease in the

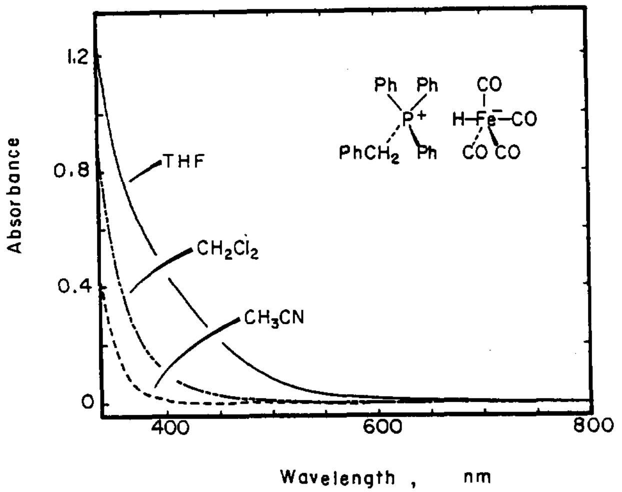

Fig. 1. Visible absorption spectrum of 1.5×10^{-3} *M* $Ph_3PCH_2Ph^+HFe(CO)_4^-$ in THF (———), CH_2Cl_2 (— - - —) and CH_3CN (- - - - - -) at 23°C.

magnitudes of $\lambda_{0.1}$ in the order THF > CH_2Cl_2 > CH_3CN for every salt. Moreover, in a given solvent, the values of $\lambda_{0.1}$ consistently decreased in Table 1 (down each column) as the carbonylmetalate was successively changed from $Mn(CO)_5^-$, $HFe(CO)_4^-$ to $Co(CO)_4^-$, in accord with the trend in their donor strengths (*vide infra*).

Salt effects on the charge-transfer spectra

Addition of small amounts of the inert salt tetra-n-butylammonium tetra-n-butylborate (TBAB) to THF solutions of carbonylmetalate salts consistently resulted in a dramatic bleaching of the yellow colors. Thus the successive addition of TBAB to a dilute (1.5×10^{-3} *M*) solution of $Ph_4P^+Mn(CO)_5^-$ resulted in the concomitant linear reduction of the absorbance at $\lambda = 500$ nm. Yellow solutions of $Ph_4P^+Co(CO)_4^-$ and $Ph_4P^+HFe(CO)_4^-$ could be similarly bleached by the addition of inert salt. In each case, the characteristic carbonyl bands of the carbonyl-

Table 1

Solvatochromism of the charge-transfer absorption bands of phosphonium carbonylmetalates [a]

Cationic acceptor	Anionic donor	$\lambda_{0.1}$ [b] THF	CH_2Cl_2	CH_3CN
Ph_4P^+	$Mn(CO)_5^-$	500	450	410
Ph_4P^+	$HFe(CO)_4^-$	470	410	390
Ph_4P^+	$Co(CO)_4^-$	430	400	360
$Ph_3PCH_2Ph^+$	$HFe(CO)_4^-$	490	400	360

[a] As 1.5×10^{-3} *M* solutions at 23°C of the crystalline charge-transfer salt. [b] Wavelength (nm) at which the absorbance reached a value of 0.1 for 1.5×10^{-3} *M* solutions in the solvents listed.

Table 2

Infrared spectra (ν(CO)) of carbonylmetalate salts [a]

Anion (symmetry) [b]	ν(CO) (cm^{-1}) Solid [c]	THF	CH_2Cl_2	CH_3CN	H_2O [d]	Assignment
$HFe(CO)_4^-$	1998	1998	2003	2004	2015	A_1
(C_{3v})	1916	1907	1913	1915	1937	A_1
	1862	1877	1878	1882	1897	E
$Mn(CO)_5^-$	1895	1895	1902	1902	1898	A_2''
(D_{3h})	1862	1861	1860	1865	1863	E'
$Co(CO)_4^-$	1873	1884	1891	1891	1915	T_2
(T_d)						

[a] As 1.5×10^{-3} M solutions of the tetraphenylphosphonium salts at 23°C in the solvent listed, unless otherwise indicated. [b] Idealized symmetry established by X-ray crystallography for $HFe(CO)_4^-$ [33b], $Mn(CO)_5^-$ [33a] and $Co(CO)_4^-$ [32]. [c] Nujol mull of the crystalline salt. [d] Aqueous solution of sodium salt [22].

metalates (see below) persisted unchanged in the IR spectrum. The latter thus identified the effect of added salt with the ionic exchange [11] such as

$$\underset{\text{(orange)}}{Ph_4P^+Mn(CO)_5^-} + Bu_4N^+BBu_4^- \rightleftharpoons Ph_4P^+BBu_4^- + \underset{\text{(colorless)}}{Bu_4N^+Mn(CO)_5^-} \tag{1}$$

Such a metathetical exchange effectively served to nullify the visible charge-transfer interaction in the contact ion pair.

Infrared spectrum of charge-transfer salts

The crystalline phosphonium salt $Ph_4P^+Co(CO)_4^-$ showed a single carbonyl band at $\nu(CO) = 1873$ cm^{-1} consistent with the infrared-allowed T_2 mode expected for $Co(CO)_4^-$ with ideal tetrahedral (T_d) symmetry. The results in Table 2 show that the same single vibrational mode for $Ph_4P^+Co(CO)_4^-$ persisted in THF, CH_2Cl_2, and CH_3CN solutions. Similarly, the pair of bands (A_2'' and E') in the carbonyl spectrum of $Ph_4P^+Mn(CO)_5^-$ and the three carbonyl bands ($2A_1$ and E) in $Ph_4P^+HFe(CO)_4^-$ that were consistently obtained in the solid state and in solution correspond to the IR-allowed ν(CO) modes calculated for D_{3h} and C_{3v} symmetries, respectively [21]. Also notable in Table 2 is the essential identity of the carbonyl bands of the organometallic salts as contact ion pairs in THF solution (column 3) with those previously observed (column 6) as free anions from the sodium carbonylmetalates in aqueous solution [22]. We conclude from the carbonyl spectra consistent with the highest possible symmetry of $Co(CO)_4^-$, $Mn(CO)_5^-$ and $HFe(CO)_4^-$, together with their essential identity in the solid state and in nonpolar media, that the charge-transfer salts always exist as separate, intact pairs of ions.

Carbonylmetalate anions and onium cations as electron donors and acceptors

The various phosphonium and sulfonium cations were evaluated as electron acceptors by electrochemical reduction at a platinum electrode in acetonitrile solution [23]. The cyclic voltammogram of tetraphenylphosphonium showed an irreversible cathodic wave at $E_p^c = -2.34$ V *vs.* ferrocene at a scan rate of 200 V s^{-1} [24,25]. The coupled anodic wave E_p^a on the return scan could only be observed at $v \geqslant 4000$ V s^{-1}, and the average $(E_p^c + E_p^a)/2 = -2.40$ V *vs.* Cp_2Fe

Table 3

Cyclic voltammetric peak-potentials of carbonylmetalate donors and onium acceptors [a]

Cation	E_p^c [b]	Anion	E_p^a [c]
Ph_4P^+	−2.34 [d]	$Co(CO)_4^-$	−0.05
$Ph_3PCH_2Ph^+$	−2.28	$HFe(CO)_4^-$	−0.37
Ph_3S^+	−2.18	$Mn(CO)_5^-$	−0.40 [e]

[a] Charge-transfer salt in acetonitrile solutions containing 0.1 *M* $TBAF_6$ at $v = 0.5$ V s^{-1} and 23°C. [b] Cathodic peak potential *vs.* Cp_2Fe^+. [c] Anodic peak potential *vs.* Cp_2Fe. [d] $E_{1/2} = -2.40$ V at $v = 4000$ V s^{-1}. [e] $E_{1/2} = -0.30$ V at $v = 175$ kV s^{-1} [27].

was taken as $E_{1/2}$ [26]. By comparison, the cyclic voltammogram of triphenylsulfonium showed no sign of chemical reversibility, even at scan rates exceeding 50000 V s^{-1}. As such, the values of E_p^c measured at the standard scan rate of $v = 0.5$ V s^{-1} were taken to represent the acceptor strengths [23] of the various phosphonium and sulfonium cations (Table 3).

The donor strengths of the carbonylmetalates were previously evaluated by an analogous electrochemical oxidation of $Co(CO)_4^-$ and $Mn(CO)_5^-$ in acetonitrile [27]. The cyclic voltammogram of $HFe(CO)_4^-$ showed similar signs of chemical irreversibility and the value of the anodic peak potential in Table 3 was evaluated at 0.5 V s^{-1}. Accordingly, the trend in the E_p^a values, namely $Mn(CO)_5^- > HFe(CO)_4^- > Co(CO)_4^-$, is to be taken as the order of anionic donor strengths.

Photoactivation of charge-transfer salts

The charge-transfer salts listed in Table 4 remained unchanged for prolonged periods in solutions carefully protected from light and air. However, deliberate irradiation with visible light ($\lambda > 400$ nm) of $Ph_3S^+Mn(CO)_5^-$ in THF solution led to a quantitative conversion of pentacarbonylmanganate within 30 min, as judged by the disappearance of the diagnostic carbonyl bands at $\nu(CO) = 1895$ and 1861

Table 4

Charge-transfer photochemistry of phosphonium and sulfonium carbonylmetalates [a]

Cationic acceptor	Anionic donor	λ [b] (nm)	Time [c] (h)	Conversion [d] (%)	Products (yield, %) [e]
Ph_4P^+	$Mn(CO)_5^-$	400	55	< 5	$PhMn(CO)_4PPh_3$ (60) [f] $Mn_2(CO)_{10}$ (20)
	$HFe(CO)_4^-$	400	38	50	$Fe(CO)_4PPh_3$ (32) PhH (32) [g]
	$Co(CO)_4^-$	380	48	< 1	$Co_2(CO)_6(PPh_3)_2$(−) [h]
$Ph_3PCH_2Ph^+$	$HFe(CO)_4^-$	400	19	55	$Fe(CO)_4PPh_3$ (42) $PhCH_3$ (62) [g]
Ph_3S^+ [i]	$Mn(CO)_5^-$	400	0.5	100	$Mn_2(CO)_{10}$ (45) $PhMn(CO)_5$ (27) [f]

[a] As 0.02 *M* solutions of the crystal CT salt at 23°C, unless otherwise indicated. [b] Cutoff wavelength. [c] Irradiation time in hours. [d] Estimated by the decrease in $\nu(CO)$ for the anionic donors (Table 2). [e] Determined by quantitative IR spectroscopy with authentic samples unless otherwise indicated. [f] Estimated from extinction coefficients in Table 1 [36]. [g] Yield by gas chromatography. [h] Not quantified. [i] CT salt generated *in situ* from $Ph_3S^+PF_6^-$ and $PPN^+Mn(CO)_5^-$ in THF.

cm^{-1} in the IR spectrum (Table 4, entry 5). The carbonyl-containing products were readily identified by the characteristic IR spectra as the dimeric dimanganese decacarbonyl ($Mn_2(CO)_{10}$, $\nu(CO) = 2045$, 2009 and 1980 cm^{-1}) [28] and the arylated product ($PhMn(CO)_5$ [29], $\nu(CO) = 2123$, 2028 and 2007 cm^{-1}). This efficient photoreaction contrasted with the long periods of irradiation under the same conditions required to effect low conversions ($< 5\%$) of the corresponding phosphonium salt $Ph_4P^+Mn(CO)_5^-$ (Table 4, entry 1). However, a more efficient photochemistry obtained from the phosphonium salt of hydridotetracarbonylferrate. Thus the yellow solution of $Ph_3PCH_2Ph^+HFe(CO)_4^-$ upon visible irradiation at $\lambda > 400$ nm yielded the phosphine-substituted $Fe(CO)_4PPh_3$ [30] in high yields together with a roughly equimolar amount of toluene (Table 4, entry 4), *i.e.*

$$Ph_3PCH_2Ph^+HFe(CO)_4^- \xrightarrow{h\nu_{CT}} Fe(CO)_4PPh_3 + PhCH_3 \qquad (2)$$

The photoefficiency of the benzyl cleavage in eq. 2 was established by quantitative actinometry with ferrioxalate as $\Phi = 0.015$ for the production of $Fe(CO)_4PPh_3$.

An analogous phenyl cleavage was also observed in the visible irradiation of the corresponding tetraphenylphosphonium salt $Ph_4P^+HFe(CO)_4^-$ under comparable conditions. It afforded the same iron carbonyl $Fe(CO)_4PPh_3$ and benzene, but with slightly lower conversions.

$$Ph_4P^+HFe(CO)_4^- \xrightarrow{h\nu_{CT}} Fe(CO)_4PPh_3 + PhH \qquad (3)$$

By contrast, the tetraphenylphosphonium salt of tetracarbonylcobaltate underwent negligible change as indicated by the retained absorbance of the carbonyl band at 1884 cm^{-1} of $Co(CO)_4^-$. A small amount ($< 0.5\%$) of the dimeric $Co_2(CO)_6(PPh_3)_2$ was tentatively identified by its carbonyl band at 1957 cm^{-1} [31].

Thermal annihilation of charge-transfer salts

Although solutions of $Ph_4P^+Mn(CO)_5^-$ in acetonitrile were stable for prolonged periods (> 4 days) if protected from light, the corresponding sulfonium analogue was too unstable to be isolated as a crystalline charge-transfer salt. The bright yellow solution of $Ph_3S^+Mn(CO)_5^-$ was therefore prepared *in situ* by mixing a solution of $PPN^+Mn(CO)_5^-$ in THF with a slight equimolar excess of $Ph_3S^+PF_6^-$ in the dark. After half an hour, the diagnostic IR bands of $Mn(CO)_5^-$ with $\nu(CO) = 1861$ and 1894 cm^{-1} were diminished to an extent of 18% conversion, and the dimeric $Mn_2(CO)_{10}$ was found in 56% yield. The further thermal transformation of $Ph_3S^+Mn(CO)_5^-$ occurred over the course of several days to produce additional amounts of $Mn_2(CO)_{10}$, but no $PhMn(CO)_5$ ($< 2\%$).

The analogous iodonium salt $Ph_2I^+Mn(CO)_5^-$ was also too unstable to isolate in crystalline form. When $Ph_2I^+PF_6^-$ was added to a colorless solution of $PPN^+Mn(CO)_5^-$ in THF, the mixture immediately turned orange. Spectroscopic (carbonyl) analysis within 5 min, indicated the complete conversion of $Mn(CO)_5^-$ to a roughly equimolar mixture of $Mn_2(CO)_{10}$ and $PhMn(CO)_5$.

Discussion

The carbonylmetalates $Co(CO)_4^-$, $Mn(CO)_5^-$ and $HFe(CO)_4^-$ in combination with the phosphonium and sulfonium cations afford highly colored, crystalline charge-transfer salts. The visible absorption band in the electronic spectrum, such as that illustrated in Fig. 1, derives from the contact ion pair which is equivalent to the charge-transfer interaction extant in the solid state. The structure of the contact ion pair is revealed by infrared spectroscopy (Table 2) which establishes the carbonylmetalate moiety in the charge-transfer salt to exist as the undistorted $Co(CO)_4^-$, $Mn(CO)_5^-$ and $HFe(CO)_4^-$ anions with T_d, D_{3h} and C_{3v} symmetry characteristic of the free anions [32,33]. Thus the observation of the characteristic one, two and three carbonyl bands in the IR spectra of the cobalt-, manganese-, and iron-containing phosphonium salts demonstrates that the carbonylmetalates conform to their highest symmetry and exist as unperturbed anions regardless of the physical state (*i.e.*, crystal, solution, *etc.*) of the charge-transfer salt. This structural situation is in strong contrast to the extensive distortion of carbonylmetalate anions previously observed when ion-paired with various pyridinium cations [11]. Since the ready deformations of these nonplanar carbonylmetalates are sensitively probed by changes in the carbonyl (IR) spectra, the ion-pair structures of charge-transfer salts can be classified into inner-sphere and outer-sphere prototypes. According to this designation, the charge-transfer salts of $Co(CO)_4^-$ paired with cyanopyridinium ($CNPy^+$) and cobaltocenium (Cp_2Co^+) cations are constituted as inner-sphere ion pairs owing to its distortion from T_d symmetry in the free anion to C_s and C_{2v} symmetry in the blue $CNPy^+Co(CO)_4^-$ and the red $Cp_2Co^+Co(CO)_4^-$, respectively [11]. By the same token, $Co(CO)_4^-$ paired with either the tetraphenylphosphonium or the triphenylsulfonium cation is to be classified as an outer-sphere charge-transfer salt owing to the presence of the anionic donor with undistorted tetrahedral symmetry. Part of the difference is undoubtedly due to the tetrahedral structure of the phosphonium cation. Since the sulfonium ion is almost planar, an additional factor that limits these onium salts to outer-sphere structures may be ascribed to the steric size of the cationic acceptor. In both instances, the interionic separation in the contact ion pair will be reflected in the charge-transfer absorption bands ($h\nu_{CT}$) associated with the unique colors of the salts. Thus the application of the Mulliken formulation to salts leads to the expression [19]

$$h\nu_{CT} = IP - EA + \omega + \text{constant} \tag{4}$$

where IP is the ionization potential of the donor anion and EA is the electron affinity of the acceptor cation. The electrostatic energy ω inherent to ion pairs is, in the limit of simple coulombic forces, inversely related to the interionic separation. Since the ionization terms (IP − EA) can be equated to the redox potentials of the donor and acceptor pairs, *i.e.*, $\mathscr{F}(E_p^c + E_p^a)$ in Table 3, the colors of the charge-transfer salts also reflect the separation in various ion-pair structures.

The relatively large interionic separations in the charge-transfer salts of carbonylmetalates with phosphonium and sulfonium cations are manifested by the blue shifts of the CT absorption bands such that only the low-energy tail (< 450 nm) is observed (Fig. 1). By comparison, the corresponding pyridinium and cobalticenium salts show well-defined charge-transfer bands with $\lambda_{max} \sim 550$ nm [11]. An important factor that contributes to the blue shift is the reduction potentials E_p^c of phosphonium and sulfonium salts which are roughly one volt more negative than that of pyridinium and cobalticenium cations. Indeed, were it not for the yellow color of $Ph_4P^+Co(CO)_4^-$ (in contrast to the colorless

$Na^+Co(CO)_4^-$ and $PPN^+Co(CO)_4^-$) [34], the charge-transfer phenomenon arising from contact ion pairs would have probably remained unnoticed.

Despite the highly endergonic energy change in eq. 4 for phosphonium and sulfonium salts, the charge-transfer interaction prevalent in the salts gives rise to a rich photochemistry under conditions in which the pyridinium and cobalticenium salts are essentially photostable [11]. It is thus noteworthy that the deliberate irradiation of $Ph_4P^+Mn(CO)_5^-$ with visible light (filtered to excite only the low-energy tail of the charge-transfer band) produces the same arylation product previously obtained [35] with UV light, *i.e.*

$$Ph_4P^+Mn(CO)_5^- \xrightarrow[\text{THF}]{h\nu_{CT}\text{ or }h\nu_{UV}} Ph\text{-}Mn(CO)_4PPh_3 + CO \qquad (5)$$

Since no photoreaction is observed when the same salt is irradiated in acetonitrile, it appears that contact ion pairs are essential for the efficient photolytic conversion of the charge-transfer salts even if only the local (UV) band is irradiated [36].

The photo-induced arylation in eq. 5 is reminiscent of the thermal reaction [37] of tetraphenylphosphonium with powerful anionic nucleophiles such as

$$Ph_4P^+ + CpFe(CO)_2^- \rightarrow PhFe(CO)_2Cp,\ [CpFe(CO)_2]_2,\ etc. \qquad (6)$$

In this connection, the common occurrence of hydrocarbylmetal carbonyls and dimeric carbonylmetals amongst the products listed in Table 4, suggests that the thermal reactions of charge-transfer ion pairs as presented in eq. 6 and the photochemical processes in Table 4 may proceed via the same (or closely related) intermediates. For example, the activation of contact ion pairs by the irradiation of the charge-transfer absorption bands is known [11] to involve the production of radical pairs, *e.g.*

$$Ph_4P^+Mn(CO)_5^- \xrightarrow{h\nu_{CT}} Ph_4P^{\cdot}Mn(CO)_5^{\cdot} \qquad (7)$$

Such a photoinduced electron transfer is often dominated by the competition from back electron transfer of the radical pair (k_{-1}) to regenerate the contact ion pair. Since the diffusive separation of radical pairs occurs with lifetimes of $\sim 10^{-9}$ s [38], any process which diverts the radical pair must occur by first-order kinetics with $k_1 \geqslant 10^8$ s^{-1}. We therefore believe that the efficient CT-induced photoreactions described in Table 4 all result from the spontaneous fragmentation of labile sulfuranyl and phosphoranyl radicals [39], *i.e.*

$$Ph_3S^{\cdot} \rightarrow Ph_2S + Ph^{\cdot},\ etc. \qquad (8)$$

and

$$Ph_3PCH_2Ph^{\cdot} \rightarrow Ph_3P + PhCH_2^{\cdot} \qquad (9)$$

as deduced from earlier pulse radiolytic and photolytic studies [40,41]. If so, the arylation of pentacarbonylmanganate can occur by homolytic combination [42] of the 17-electron radical fragment, *e.g.*

$$Ph_3S^+Mn(CO)_5^- \xrightarrow{h\nu_{CT}} [Ph_3S^{\cdot}, Mn(CO)_5^{\cdot}] \qquad (10)$$

$$[Ph_3S^{\cdot}, Mn(CO)_5^{\cdot}] \rightarrow [Ph_2S, Ph^{\cdot}, Mn(CO)_5^{\cdot}] \qquad (11)$$

$$[Ph_2S, Ph^{\cdot}, Mn(CO)_5^{\cdot}] \rightarrow Ph_2S + PhMn(CO)_5 \qquad (12)$$

The extent to which the caged triad in eq. 11 suffers diffusion separations allows the phenyl radical to be trapped by solvent (as benzene) and the 17-electron carbonylmanganese radical to undergo dimerization to $\mathrm{Mn_2(CO)_{10}}$.

Similar homolytic combinations also apply to the radical pair from the phosphonium salt in eq. 7. However, the fragmentation of the phosphoranyl radical generates triphenylphosphine which is a highly effective σ-donor that is capable of effecting ligand substitution of the labile 17-electron radical [43] within the caged triad, *e.g.*

$$\mathrm{Ph_4P^{\cdot+}Mn(CO)_5^-} \xrightarrow{h\nu_{\mathrm{CT}}} \left[\mathrm{Ph_4P^{\cdot}, Mn(CO)_5^{\cdot}}\right] \tag{13}$$

$$\left[\mathrm{Ph_4P^{\cdot}, Mn(CO)_5^{\cdot}}\right] \rightarrow \left[\mathrm{Ph_3P, Ph^{\cdot}Mn(CO)_5^{\cdot}}\right] \tag{14}$$

$$\left[\mathrm{Ph_3P, Ph^{\cdot}, Mn(CO)_5^{\cdot}}\right] \rightarrow \left[\mathrm{Ph^{\cdot}, Mn(CO)_4PPh_3^{\cdot}, CO}\right] \tag{15}$$

$$\left[\mathrm{Ph^{\cdot}, Mn(CO)_4PPh_3^{\cdot}, CO}\right] \rightarrow \mathrm{PhMn(CO)_4PPh_3 + CO} \tag{16}$$

In an analogous manner, the organometallic cleavage of the hydridoferrate salts in eqs. 2 and 3 could result from the hydrogen atom transfer from the reactive 17-electron radical (eq. 18) followed by ligation of the coordinatively unsaturated 16-electron tetracarbonyliron(0) species, *i.e.*

$$\left[\mathrm{Ph_3PCH_2Ph^{\cdot}, HFe(CO)_4^{\cdot}}\right] \rightarrow \left[\mathrm{Ph_3P, PhCH_2^{\cdot}, HFe(CO)_4}\right] \tag{17}$$

$$\left[\mathrm{Ph_3P, PhCH_2^{\cdot}, HFe(CO)_4^{\cdot}}\right] \rightarrow \left[\mathrm{Ph_3P, PhCH_3, Fe(CO)_4}\right] \tag{18}$$

$$\left[\mathrm{Ph_3P, PhCH_3, Fe(CO)_4}\right] \rightarrow \mathrm{PhCH_3 + Ph_3PFe(CO)_4} \tag{19}$$

However, the low quantum yield of $\Phi = 0.015$ for the photoreaction in eq. 2 indicates that the overall process is still dominated by back electron transfer from the first-formed radical pair. We hope that time-resolved spectroscopic studies presently in progress will provide additional mechanistic information on the reactive (radical) intermediates responsible for the photoactivation of charge-transfer salts.

The photochemical activation of the phosphonium salt $\mathrm{Ph_4P^+Mn(CO)_5^-}$ has its thermal counterpart in the facile (dark) conversion of the iodonium salt $\mathrm{Ph_2I^+Mn(CO)_5^-}$ and, to a lesser extent, the sulfonium salt $\mathrm{Ph_3S^+Mn(CO)_5^-}$. The absence of a thermal reaction of the phosphonium salt is consistent with a highly endergonic driving force $-\Delta G \leqslant -2$ eV for electron transfer (*cf.* eq. 7) that can be approximated by the CV peak potentials in Table 3 as $\Delta G \simeq (E_{\mathrm{p}}^{\mathrm{c}} + E_{\mathrm{p}}^{\mathrm{a}})$ [44]. By comparison, the driving force for electron transfer in the corresponding iodonium salt is close to isoergonic based on a reduction potential for $\mathrm{Ph_2I^+}$ that is roughly 0 V [45], *i.e.*

$$\mathrm{Ph_2I^+Mn(CO)_5^-} \xrightarrow{\Delta G \approx 0} \mathrm{Ph_2I^{\cdot}, Mn(CO)_5^{\cdot}} \tag{20}$$

As such, the rate of ion-pair annihilation in eq. 20 is expected to be rapid and to generate a high instantaneous flux of phenyl and $\mathrm{Mn(CO)_5}$ radicals. The latter can be responsible for the relatively high yields of $\mathrm{PhMn(CO)_5}$ as a result of radical coupling (see eq. 12). By contrast, the more endergonic driving force of $\Delta G \sim 1.5$ eV for the annihilation of the sulfonium salt $\mathrm{Ph_3S^+Mn(CO)_5^-}$ will lead to a slower rate of electron transfer and allow the diffusive separation of the radical pair. The latter is consistent with the high yield of $Mn_2(CO)_{10}$ arising from the coupling of the relatively long-lived 17-electron radical [27]. We hope that additional studies of ion-pair annihilation in progress will shed further light on this formulation.

Experimental section

Materials

Tetraphenylphosphonium bromide (Aldrich), triphenylbenzylphosphonium (Cincinnati Milacron) and triphenylsulfonium chloride (Aldrich) were converted to the corresponding hexafluorophosphate salt by precipitation from an aqueous solution of $NH_4^+PF_6^-$ [46]. The tetraphenylphosphonium salts of $Mn(CO)_5^-$ and $HFe(CO)_4^-$ were prepared as described [36,47]. Tetraphenylphosphonium tetracarbonylcobaltate was prepared from 0.1 *M* $NaCo(CO)_4$ [34] in water by treatment with an equimolar amount of $Ph_4P^+Br^-$ under anaerobic conditions. The bright yellow precipitate was dried *in vacuo* and recrystallized from a mixture of THF and diethyl ether to yield 3.7 g (73%) of bright yellow needles. Anal. calcd. for $C_{28}H_{20}CoO_4P$: C, 65.88; H, 3.95. Found (by Atlantic Microlabs, Norcross, GA): C, 65.90; H, 3.95%. The crystalline $Fe(CO)_4PPh_3$ for IR calibration was purified by column chromatography on silica gel with hexane as the eluent. Dimanganese decacarbonyl (Strem) was purified by sublimation *in vacuo*.

Tetrahydrofuran (reagent grade, Fisher) was distilled from sodiobenzophenone and stored in a Schlenk flask under an argon atmosphere. Acetonitrile was distilled successively from potassium permanganate, phosphorus pentoxide and calcium hydride under an argon atmosphere. Dichloromethane was treated with conc. H_2SO_4, predried over anhydrous $CaCl_2$ and distilled from calcium hydride under an argon atmosphere. All manipulations of the purified charge-transfer salts were carried out with Schlenk techniques under an argon atmosphere.

Instrumentation

Infrared spectra were recorded on a Nicolet 10DX FT-IR spectrometer using either a 1.0 mm NaCl cell (solution) or Nujol mull (crystal) with (digital) background subtraction. UV–visible spectra were measured on a Hewlett–Packard 8450A diode-array spectrometer. Electrochemical measurements in acetonitrile solutions containing 0.1 *M* tetrabutylammonium hexafluorophosphate (Aldrich, recrystallized from ethyl acetate) as the supporting electrolyte, utilized a BAS 100A electrochemical analyzer in conjunction with an air-tight CV cell. Cyclic voltammetry at scan rates exceeding 100 V s^{-1} were carried out with platinum microelectrodes (12.5 μm radius) connected to a locally-constructed rapid-scan potentiostat employing fast response operational amplifiers (Motorola LF 357) that was driven by an Exact 628 function generator. Data storage and manipulation were carried out with a Gould Biomation 4500 digital oscilloscope. Quantitative gas chromatography was performed on a Hewlett–Packard 5790 FID gas chromatograph/3392 integrator that was based on either toluene or *m*-xylene as the internal standard.

Electronic spectra of charge-transfer salts

Spectroscopic measurements were all carried out under an atmosphere of argon in 1.0 cm quartz cuvettes equipped with Teflon valves. Solvent and salt effects on the electronic spectra of $Ph_4P^+Mn(CO)_5^-$, $Ph_4P^+HFe(CO)_4^-$ and $Ph_4P^+Co(CO)_4^-$ were determined by the procedure described previously [11]. The inert salt tetra-n-butylammonium tetra-n-butylborate (TBAB) [48] was purified by crystallization from a mixture of THF and hexane.

Charge-transfer photochemistry of contact ion pairs

Photolyses were performed with a focussed beam from a 500 W mercury lamp that was passed through an IR filter and an appropriate Pyrex sharp cutoff filter (Corning CS-3, 380 or 400 nm). The photolysis cell consisted of a 1.0 cm quartz cuvette closed with an air-tight Teflon stopcock for purging with argon. The photochemical transformations were continuously monitored by UV–visible and IR spectroscopy. The yields of the carbonylmetal products were based on quantitative IR analysis of the diagnostic carbonyl bands of authentic standards as follows.

$Ph_4P^+HFe(CO)_4^-$ was irradiated as a 0.02 *M* THF solution at $\lambda > 400$ nm until ~ 50% of the charge-transfer salt was converted. Analysis of $Fe(CO)_4PPh_3$ (32%) was established by quantitative IR spectroscopy utilizing the carbonyl band at 2048 cm^{-1}. Benzene (32%) was analyzed by gas chromatography using toluene as the internal standard. The small amount of orange precipitate showed no carbonyl absorption (1500–2200 cm^{-1}). A control experiment carried out in the dark for the same period (38 h) showed no change. After irradiation was complete, the photolysate was concentrated *in vacuo*, and the residue extracted with toluene. Column chromatography on silica gel yielded $Fe(CO)_4PPh_3$ [$\nu(CO) = 2048$ (s), 1978 (m), 1941 (s) cm^{-1}] [30].

$Ph_3PCH_2Ph^+HFe(CO)_4^-$ was similarly treated at $\lambda > 400$ nm for 19 h to effect 57% conversion. Quantification of $Fe(CO)_4PPh_3$ and toluene (*m*-xylene internal standard) as described above indicated 42% and 62%, respectively. The control experiment in the dark showed no changes in the IR spectrum.

$Ph_4P^+Mn(CO)_5^-$ was irradiated at $\lambda > 400$ nm for 55 h to yield $PhMn(CO)_4PPh_3$ (3.2%, 2064 cm^{-1}, ϵ 2160 [36]), $Mn_2(CO)_{10}$ (1.0%, 2045 cm^{-1}) and traces of $PhMn(CO)_5$.

$Ph_4S^+Co(CO)_4^-$ showed essentially no change at $\lambda > 380$ nm for 24 h.

$Ph_3S^+Mn(CO)_5^-$ prepared *in situ* from 0.015 mmol $PPN^+Mn(CO)_5^-$ and 9 mg $Ph_3S^+PF_6^-$ in 5 mL of THF was irradiated at $\lambda > 400$ nm for ~ 30 min. The complete conversion of the charge-transfer salt (1861, 1894 cm^{-1}) resulted in 44% $Mn_2(CO)_{10}$ and 27% $PhMn(CO)_5$. A slow dark reaction (18%) occurred in the same period to give $Mn_2(CO)_{10}$.

Quantum yields for charge-transfer photochemistry

A 450-W xenon lamp equipped with a narrow band interference filter (400 ± 5 nm) was employed as the monochromatic light source, the intensity of which was calibrated with a ferrioxalate actinometer [49]. A 0.1 *M* solution of $Ph_3PCH_2Ph^+HFe(CO)_4^-$ in THF was irradiated for 4 h, and the yield of $Fe(CO)_4PPh_3$ established by quantitative IR spectroscopy (see above).

Thermal annihilation of charge-transfer salts

Solid sulfonium salt $Ph_3S^+PF_6^-$ (9 mg, 0.02 mmol) was added to a stirred solution of $PPN^+Mn(CO)_5^-$ (11 mg, 0.015 mmol) in 5 mL of THF at 22°C under an argon atmosphere. The solution immediately turned deep yellow and after stirring in the dark for 0.5 h, an aliquot of the solution was reserved for IR analysis. The concentration of $Mn(CO)_5^-$ was found by spectrophotometry of the carbonyl bands at 1894 and 1861 cm^{-1} to be 2.45×10^{-3} *M* (corresponding to 18% conversion). The dimeric $Mn_2(CO)_{10}$ was present in 1.5×10^{-4} *M* (56% yield) as determined from the intensity of the carbonyl band at 2045 cm^{-1}. A further transformation (35%) of $Mn(CO)_5^-$ was effected upon standing for 4 days in the dark.

Iodonium salt $Ph_2I^+Mn(CO)_5^-$ (5 mg, 0.012 mmol) was added as a solid to a solution of $PPN^+Mn(CO)_5^-$ (6 mg, 0.008 mmol) in 4 mL of THF at 22°C to afford immediately a deep red solution. The homogeneous mixture was stirred for 5 min and an aliquot recovered for IR analysis. The characteristic carbonyl bands of $Mn(CO)_5^-$ were absent and replaced with the carbonyl bands at 2045, 2015 and 1983 cm^{-1} of $Mn_2(CO)_{10}$ in 54% yield and 2114, 2053, 2013 and 1993 cm^{-1} of $PhMn(CO)_5$ in approximately 38% yield.

A solution of $Ph_4P^+Mn(CO)_5^-$ (30 mg, 0.058 mmol) in 3 mL of THF was stirred in the dark at 22°C under an atmosphere of argon for 2 days. IR analysis showed that the concentration of $Mn(CO)_5^-$ (ν(CO) = 1894 and 1861 cm^{-1}) was undiminished.

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