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Disproportionation Reactions of the Dimeric Allyliron Compound $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$; Formation of Novel Cationic η^3-Allylironcarbonyl Complexes

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Abstract

The metal–metal bonded dimer $[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2$ disproportionates on treatment with a variety of tertiary phosphines, forming the ionic allyl iron complexes $[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2][(\eta^3\text{-}C_3H_5)Fe(CO)_3]$ (L = PMe_3, PEt_3, PMe_2Ph, $PMePh_2$, PPh_3). The iron(0) anionic complex has been reported previously but not the labile, iron(II) cationic complexes, which are better synthesized by treatment of $(\eta^3\text{-}C_3H_5)Fe(CO)_3Br$ with the tertiary phosphines.

Introduction

There is currently great interest in the chemistry of seventeen-electron organotransition metal compounds, which have often been synthesized via either photochemically induced homolysis of metal–metal bonded, eighteen-electron dimeric species [1] or electron transfer reactions of eighteen-electron monomers [2]. Most seventeen-electron complexes resemble organic radicals in that they are very unstable with respect to dimerization, and readily take part in a variety of ligand substitution and atom abstraction reactions [3].

Interestingly, the metal–metal bond of the compound $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ is very long (3.281(1) Å) [4] and weak (≈12.7 kcal mol^{-1} [5], and it has been recently established that low but chemically significant concentrations of the monomeric, metal-centred radical $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$ exist in solution in equilibrium with the dimer [6, 7]. Indeed, we have recently demonstrated that the solution chemistry of the dimer reflects the reactivity of the monomer, and a number of ligand substitution, disproportionation and atom abstraction reactions of $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$, the related $\{(\eta^5\text{-}C_5Me_5)Cr(CO)_3\}$ and similar molybdenum species have been investigated [7–12].

Similar to the chromium system, the binuclear complex $[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2$ also exhibits a very long metal–metal bond (3.138(3) Å) [13] and dissociates in solution to give the paramagnetic species $\{(\eta^3\text{-}C_3H_5)Fe(CO)_3\}$, as in eqn. (1) [14, 15].

$$[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2 \rightleftharpoons 2\{(\eta^3\text{-}C_3H_5)Fe(CO)_3\} \quad (1)$$

As with the above-mentioned chromium system [10], the seventeen-electron monomer is very labile, and substition of carbon monoxide by various phosphines results in the formation of the substituted species $[(\eta^3\text{-}C_3H_5)Fe(CO)_2L]_n$ (n = 1, 2; L = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3) [14, 15]. The substituted compounds are much more extensively dissociated in solution than is the tricarbonyl dimer, and have been characterized by IR and ESR spectroscopy [14, 15].

In parallel with our investigations of the chromium and molybdenum radical systems [7–12], we have initiated an analogous study of the allyliron radicals. The chemistry of the substituted monomeric radical species has been little explored, and we hoped also to be able to carry out X-ray crystallographic and single crystal ESR spectroscopic studies on one or more compounds. Surprisingly, however, during attempts to duplicate previously reported syntheses [14, 15], it was found that reactions of the compound $[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2$ with tertiary phosphines L yielded not only the expected radicals, $\{(\eta^3\text{-}C_3H_5)Fe(CO)_2L\}$, but also the products of disproportionation, $[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2][(\eta^3\text{-}C_3H_5)Fe(CO)_3]$. Neither the disproportionation reactions nor the complex cations have been previously described, either in this or any other context. We therefore report here details on both, and speculate on why the cationic complexes have not heretofore been synthesized.

Experimental

IR spectra were recorded on a Bruker IFS-85 FT IR spectrometer, ^1H, and $^{31}P\{^1H\}$ NMR spectra on a Bruker AM 400 spectrometer; the IR, ^1H and $^{31}P\{^1H\}$ spectra are reported in Tables 1–3, respectively. Chemical shifts are reported in δ (ppm) relative to internal TMS for ^1H, to external H_3PO_4 for

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TABLE 1. IR data

Complex	ν(CO) (cm^{-1})
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_3\}$	2043, 1963 (ether)
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_2(PMe_3)\}$	1960, 1884 (ether)
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_2(PEt_3)\}$	1960, 1885 (ether)
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_2(PMePh_2)\}$	1963, 1899 (ether)
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_2(PMe_2Ph)\}$	1961, 1895 (ether)
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_2(PPh_3)\}$	1968, 1902 (ether)
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2(PMe_3)_2]^+$	2012, 1954 (Nujol)
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2(PEt_3)_2]^+$	2017, 1960 (Nujol)
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2(PMePh_2)_2]^+$	2015, 1959 (Nujol)
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2(PMe_2Ph)_2]^+$	2020, 1967 (Nujol)
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2(PPh_3)_2]^+$	2009, 1958 (Nujol)

TABLE 2. ^1H NMR data for the complexes $[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2]^+$ in CD_2Cl_2 [a]

Ligand L	δ ^1H
$PMePh_2$	δ1.61 (br q, H_a), δ1.91 (br, PMe), δ2.13 (br, PMe), δ2.99 (d, $J(H_cH_s)$ = 7 Hz, H_s), δ4.25 (m, H_c), δ5.83–7.62 (m, Ph)
PMe_2Ph	δ1.67 (br q, H_a), δ1.78 (d, J(PH) = 9.5 Hz, PMe), δ2.04 (d, J(PH) = 9 Hz, PMe), δ2.90 (d, $J(H_cH_s)$ = 7 Hz, H_s), δ4.10 (m, H_c), δ5.84–7.70 (m, Ph)
PMe_3	δ1.33 (m, PMe), δ1.55 (m, PMe), δ1.67 (br q, H_a), δ3.29 (m, H_s), δ4.54 (m, H_c)
PEt_3	δ0.95–1.77 (m, PEt), δ2.30, (br q, H_a), δ3.13 (br d, $J(H_aH_b)$ = 8 Hz, H_s), δ4.33 (br m, H_c)

[a] As the tetraphenylborate salts.

TABLE 3. ^{31}P NMR data for the complexes $[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2]^+$ in CD_2Cl_2

Ligand L	δ ^{31}P	J(PP) (Hz)
PMe_3 [a]	33(d)	76.1
	16(d)	75.4
PEt_3 [a]	53(d)	68.7
	42(d)	68.7
PEt_3 [b]	53(d)	67.8
	42(d)	67.4
PMe_2Ph [a]	44(d)	79.3
	30(d)	79.3
PMe_2Ph [b]	38(d)	78.3
	24(d)	77.8
$PMePh_2$ [a]	52(d)	75.5
	46(d)	75.0
$PMePh_2$ [b]	49(d)	76.1
	43(d)	76.8

[a] Anion = $[(\eta^3\text{-}C_3H_5Fe(CO)_3]^-$. [b] Anion = BPh_4^-.

TABLE 4. Mass spectral data for the complexes $[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2]BPh_4$

L, Complex ion	Mass/charge	Relative abundance (%)
PMe_3		
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2]^+$	305.1	33
$[Fe(CO)_2L_2]^+$	264.0	23
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2L]^+$	229.1	26
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2]^+$	152.1	6
$[(\eta^3\text{-}C_3H_5)Fe(CO)L_2]^+$	277.1	4
$[(\eta^3\text{-}C_3H_5)FeL_2]^+$	249.1	38
$[(\eta^3\text{-}C_3H_5)Fe(CO)L]^+$		
$[(\eta^3\text{-}C_3H_5)FeL]^+$	173.0	31
$[(\eta^3\text{-}C_3H_5)Fe]^+$		
$[FeL]^+$		
PEt_3		
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2]^+$	389.1	100
$[Fe(CO)_2L_2]^+$		
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2L]^+$	271.1	5
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2]^+$	152.1	4
$[(\eta^3\text{-}C_3H_5)Fe(CO)L_2]^+$	361.2	6
$[(\eta^3\text{-}C_3H_5)FeL_2]^+$	333.2	45
$[(\eta^3\text{-}C_3H_5)Fe(CO)L]^+$		
$[(\eta^3\text{-}C_3H_5)FeL]^+$	215.1	40
$[(\eta^3\text{-}C_3H_5)Fe]^+$		
$[FeL]^+$		
PMe_2Ph		
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2]^+$	429.2	23
$[Fe(CO)_2L_2]^+$		
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2L]^+$		
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2]^+$		
$[(\eta^3\text{-}C_3H_5)Fe(CO)L_2]^+$	401.2	4
$[(\eta^3\text{-}C_3H_5)FeL_2]^+$	373.2	29
$[(\eta^3\text{-}C_3H_5)Fe(CO)L]^+$	263.1	12
$[(\eta^3\text{-}C_3H_5)FeL]^+$	235.1	15
$[(\eta^3\text{-}C_3H_5)Fe]^+$		
$[FeL]^+$	194.1	5
$PMePh_2$		
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2]^+$	553.1	8
$[Fe(CO)_2L_2]^+$		
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2L]^+$		
$[(\eta^3\text{-}C_3H_5)Fe(CO)_2]^+$		
$[(\eta^3\text{-}C_3H_5)Fe(CO)L_2]^+$		
$[(\eta^3\text{-}C_3H_5)FeL_2]^+$	497.2	7
$[(\eta^3\text{-}C_3H_5)Fe(CO)L]^+$	325.1	11
$[(\eta^3\text{-}C_3H_5)FeL]^+$	297.1	11
$[(\eta^3\text{-}C_3H_5)Fe]^+$		
$[FeL]^+$	256.0	11

^{31}P. FAB mass spectral analyses were carried out at the McMaster University Regional Centre for Mass Spectrometry on a VG ZAB-E mass spectrometer; the data are reported in Table 4.

All reactions were carried out under oxygen-free nitrogen using dried, de-aerated solvents. The compounds $(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\text{Br}$ and $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3]_2$ were synthesized as in the literature [13]. The dimer was normally used *in situ*, having been synthesized from the bromo compound in ethyl ether or toluene, depending on the solvent desired for subsequent reactions.

Reactions of $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3]_2$ with Tertiary Phosphines

As a general procedure, $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3]_2$ was synthesized from $(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\text{Br}$ (0.30 g, 1.15 mmol) via zinc reduction in approximately 50 ml ether or toluene. On the addition of two equivalents of phosphine (2.30 mmol) in approximately 10 ml solvent to the solution of the dimer, the deep red solution changed to dark green, gas was evolved and, in the case of reactions carried out in ethyl ether, precipitates of the orange–yellow products, $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{L}_2][(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3]$ (L = PPh_3, PPh_2Me, PPhMe_2, PMe_3, PEt_3) formed. The solid disproportionation products were collected by filtration, washed with ether and hexanes, and dried *in vacuo*; yields were 28–36%.

As expected, the same cationic complexes $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{L}_2]^+$ can be synthesized by treating $(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\text{Br}$ with the phosphines, and this route was utilized to synthesize samples for mass spectroscopic characterization. Typically, $(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\text{Br}$ (0.40 g, 1.5 mmol) was dissolved in approximately 20 ml ethanol. To this were added 2 equivalents of phosphine (3.0 mmol) in 10 ml ethanol, at which time gas evolution occurred and the colour of the solution changed from brown to orange. The solution was reduced to a volume of approximately 10 ml and a twofold excess of NaBPh_4 in 15 ml of ethanol was added. The volume was reduced again to approximately 15 ml and the resulting light yellow product, $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{L}_2]\text{BPh}_4$, was collected on a frit, washed with ether and dried *in vacuo*. Yields were typically 60–85%.

Results and Discussion

Murdoch and Lucken have reported that $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3]_2$ reacts with PPh_3 to form the substituted monomer $\{(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2(\text{PPh}_3)\}$, although details of the reaction conditions are unclear [14]. Similarly, Muetterties *et al.* have utilized ESR spectroscopy to monitor the reactions of $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3]_2$ with PMe_3, PMe_2Ph, PMePh_2 and PPh_3 in pentane and toluene, finding evidence for the formation of ESR-active species, presumably of the type $\{(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{L}\}$ since hyperfine coupling to a single phosphorus nucleus was observed [15]. On the basis of the temperature dependencies of the ESR signals and, apparently, assuming that all diamagnetic materials were present in solution as the diamagnetic, dimeric compounds $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{L}]_2$, thermodynamic data for the monomer–dimer equilibria (eqn. (2)) were determined [15].

$$[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{L}]_2 \rightleftharpoons 2\{(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{L}\} \tag{2}$$

While attempting to obtain pure, crystalline samples of the radicals $\{(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{L}\}$ in ethyl ether and toluene, however, we have found that the reactions are not adequately described by eqn. (2). In ether, with PPh_3, PPh_2Me, PPhMe_2, PMe_3, PEt_3, up to 30% of the starting material was converted to the products of disproportionation, $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{L}_2][(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3]$; in several cases, these ionic products precipitated from solution and could be isolated and characterized spectroscopically although none was sufficiently thermally stable to be obtained analytically pure. Thus, for L = PMe_3, PEt_3, PMe_2Ph and PMePh_2, broad ν(CO) for the anion were observed at 1930 ± 8 and 1860 ± 10 cm^{-1} (Nujol, methylene chloride, ethyl ether), at much lower frequencies than the ν(CO) of the cationic counterions (see below), but comparable to ν(CO) for the analogous sodium salt (1910, 1855 cm^{-1} in THF [16]). The ^{1}H NMR resonances of the complex anion were evident in the region δ 1–2, generally upfield of the allylic ^{1}H resonances of the complex cations but obscured in large part by resonances of the tertiary phosphines and thus unassignable [16]*. Yields of the ionic products were much lower in toluene, but they were still observed in all cases as orange, crystalline precipitates on the walls of the reaction flasks.

Examination of the IR spectra of the reaction solutions in the ν(CO) region demonstrated for all five phosphines the presence of the monomeric radicals $\{(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{L}\}$ (Table 1), identified by comparisons with literature data for the PPh_3 and P(n-Bu)_3 compounds [14]. In addition, for the reactions of PMe_3 and PEt_3 in ethyl ether and PMePh_2 in toluene, at least, weak ν(CO) for the disproportionation products were observed (Table 1), but in no case were there observed any ν(CO) which could be attributed to dimeric species of the type $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_2\text{L}]_2$. It seems unlikely that the ν(CO) for the dimers would totally overlap with and be obscured by ν(CO) for the monomers; certainly the tricarbonyl monomer and dimer, $\{(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3\}$ and $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3]_2$, exhibit significantly different IR spectra in the ν(CO) region [14]. Similarly, the dimeric $[(\eta^5\text{-C}_5\text{H}_5\text{Cr(CO)}_3]_2$ and $[(\eta^5\text{-C}_5\text{Me}_5\text{Cr(CO)}_3]_2$ exhibit ν(CO) significantly different from the ν(CO) of the corresponding monomers [6, 11]. Although, as

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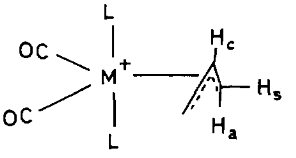
*The synthesis of $\text{Na}[\eta^3\text{-C}_3\text{H}_5\text{Fe(CO)}_3]$ outlined in this paper does not give pure product, as shown by the IR spectrum. However, the ^{1}H NMR spectrum of the product does exhibit multiplets in the region δ 1–2, consistent with our assignments.

mentioned above, substituted dimeric complexes were assumed to be present in a thermodynamic study, monitored by ESR spectroscopy, of the chemistry represented by eqn. (2) [15], we note that confirmation of the putative dimeric species was not obtained via IR spectroscopy in this earlier work.

Although all attempts to obtain the new cationic complexes $[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2]^+$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3) analytically pure (as the $\eta^3\text{-}C_3H_5)Fe(CO)_3^-$ or BPh_4^- salts) failed because of their general thermal lability (all decomposed in solution to complexes of the types $Fe(CO)_4L$ and $Fe(CO)_3L_2$), the formulations have been unambiguously established via spectroscopic techniques. Thus FAB mass spectra of the tetraphenylborate salts, $[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2]BPh_4$, exhibited peaks for the parent ions of the cations $[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2]^+$, as well as peaks for the species $[Fe(CO)_2L_2]^+$, $[(\eta^3\text{-}C_3H_5)Fe(CO)_2L]^+$, $[(\eta^3\text{-}C_3H_5)Fe(CO)_2]^+$, $[(\eta^3\text{-}C_3H_5)Fe(CO)L_2]^+$, $[(\eta^3\text{-}C_3H_5)FeL_2]^+$, $[(\eta^3\text{-}C_3H_5)Fe(CO)L]^+$, $[(\eta^3\text{-}C_3H_5)FeL]^+$, $[(\eta^3\text{-}C_3H_5)Fe]^+$ and $[FeL]^+$ (Table 4).

By analogy with isoelectronic manganese complexes of the general formula $(\eta^3\text{-}C_3H_5)Mn(CO)_2L_2$ [17, 18], the structures of the new complex cations should be as shown in A.



A

(M = Fe; L = PMe_3, PEt_3, PMe_2Ph, $PMePh_2$, PPh_3)

Two ν(CO) are observed in the IR spectra of each of the cationic complexes, implying *cis* dispositions of carbonyl groups (Table 1), but detailed interpretations of the ^1H NMR spectra (Table 2) of the new cationic complexes were difficult because of the above-mentioned thermal lability. However, the allyl protons exhibit chemical shifts comparable with those of the complexes $(\eta^3\text{-}C_3H_5)Fe(CO)_3X$ (X = Cl, Br, I) [19–21], with the resonances of the centre hydrogens (H_c) appearing as unresolved multiplets and those of the *syn* hydrogens (H_s) appearing as doublets with $J(HH) \approx 7$ Hz. The resonances of the *anti* hydrogens (H_a), on the other hand are not the simple doublets anticipated on the basis of the spectra of the compounds $(\eta^3\text{-}C_3H_5)Fe(CO)_3X$ [19–21], but are broadened quartets, presumably because of coupling to ^{31}P. The appearances of the allyl resonances are in fact very similar to those of the above-mentioned manganese analogues [17, 18], providing further evidence for structures as in A. There is, however, no evidence for the rotational isomerization exhibited by the complexes $(\eta^3\text{-}C_3H_5)Fe(CO)_3X$ [19–21].

Interestingly, the ^1H NMR spectra of the PMe_3, PMe_2Ph and $PMePh_2$ complexes each exhibit two methyl resonances, indicating that the pairs of phosphines are non-equivalent, compatible with A. Similarly, the $^{31}P\{^1H\}$ NMR spectra (Table 3) of the cationic complexes exhibit AB quartets with chemical shift differences and $^2J(PP)$ of approximately 6–17 ppm and 67–80 Hz, respectively. The chemical shift differences are thus small but consonant with the rather subtle origin of the non-equivalence of the phosphorus environments. The observed values of $^2J(PP)$ are compatible with *trans* dispositions of the phosphine ligands in the series of complexes, but we note that *cis* couplings could be of comparable magnitude [22, 23]. It was unfortunately not possible with most complexes to obtain useful ^{13}C NMR spectra because of low solubilities and/or decomposition during spectral accumulation.

Disproportionation reactions of metal–metal bonded compounds and metal-centred radicals have many precedents, and are believed in many cases to involve nineteen-electron intermediates or transition states [24]. Thus the reactions reported here presumably occur via dissociation of the dimer $[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2$ (as in eqn. (1)), followed in turn by reaction of the monomeric radical with the tertiary phosphines L and electron transfer (eqns. (3)–(5)).

$$[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2 \rightleftharpoons 2\{(\eta^3\text{-}C_3H_5)Fe(CO)_3\} \qquad (1)$$

$$\begin{tikzcd} \{(\eta^3\text{-}C_3H_5)Fe(CO)_3\} + L \arrow[r] & `\{(\eta^3\text{-}C_3H_5)Fe(CO)_3L\}' \arrow[d, "\{(\eta^3\text{-}C_3H_5)Fe(CO)_3\}"] & (3) \\ & {[(\eta^3\text{-}C_3H_5)Fe(CO)_2L]^+ + [(\eta^3\text{-}C_3H_5)Fe(CO)_3]^-} \arrow[d, "L"] & (4) \\ & {[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2]^+} & (5) \end{tikzcd}$$

It is also pertinent to ask why this hardly unusual class of cationic allyliron complexes has not been prepared previously, via either the type of disproportionation reactions reported here, or via substitution reactions of complexes of the types $(\eta^3\text{-}C_3H_5)Fe(CO)_3X$ or $[(\eta^3\text{-}C_3H_5)Fe(CO)_4]X$ (X = anion) [19–21, 25]. It would seem that disproportionation reactions have not been previously noted because earlier studies have been carried out in nonpolar solvents [14, 15] in which, as mentioned above, the ionic products $[(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2][(\eta^3\text{-}C_3H_5)Fe(CO)_3]$ are formed in very low yields. On the other hand, with respect to substitution reactions of allyl complexes of formally iron(II), it seems that a complicating factor is the proclivity of these species to undergo nucleophilic attack at the coordinated allyl group, yielding allylphosphonium salts and complexes of iron(0) [19, 25, 26]. Thus reaction of (η^3-C_3H_5)Fe(CO)$_3$I with an equimolar amount of PPh$_3$ in THF results in the formation of [P(C_3H_5)-Ph$_3$]I (31%) and (η^3-C_3H_5)Fe(CO)$_2$(PPh$_3$)I (6%), while reaction of a series of complexes of the type [(η^3-substituted allyl)Fe(CO)$_4$]$^+$ with nitrogen and phosphorus donors results in the formation of even higher yields of allylammonium and -phosphonium salts [27].

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