Neutral and cationic iron carbonyl complexes substituted with the water-soluble phosphines $[Ph_2P(CH_2)_nPMe_3]^+$ ($n = 2, 3, 6$ and 10) ☆

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Abstract

Two series of iron carbonyl complexes of the types $Fe(CO)_4L$ and $[CpFe(CO)_2L]^+$ (L = water-soluble phosphines $[Ph_2P(CH_2)_nPMe_3]^+$, $n = 2, 3, 6$ and 10, henceforth denoted as II-, III-, VI- and X-phophos respectively), containing neutral iron(0) and monocationic iron(II) centres respectively, have been prepared and characterized by mass spectroscopy, IR and multinuclear NMR techniques. In addition to the complexes $Fe(CO)_4L$, disubstituted derivatives of the type *trans*-$Fe(CO)_3L_2$ have also been obtained as byproducts. For the complex *trans*-$[Fe(CO)_3(II\text{-phophos})_2](PF_6)_2$, the II-phophos $^{31}P\{^1H\}$ resonances, formally an $XAA'X'$ spin system, exhibit virtual coupling, to our knowledge the first such example in a bis-tertiary phosphine complex in which X and X' are ^{31}P nuclei.

Keywords: Iron; Phosphine complexes; Neutral iron carbonyl; Cationic iron carbonyl; Water-soluble phosphines

1. Introduction

Investigation of the coordination properties of water-soluble phosphine ligands [1] is of practical importance since the corresponding substituted metal complexes may serve as biphasic catalysts in either liquid–liquid or solid–liquid (being anchored to an inert support) media. The utilization of biphasic catalysts is promising with respect to the ease of separation of the products from catalyst while at the same time preserving the advantageous activity and selectivity of traditional homogeneous catalysts. So far aqueous phase hydrogenation and hydroformylation of various unsaturated substrates has attracted the greatest attention [2], rhodium and cobalt complexes of various water-soluble phosphines proving to be useful catalysts as in purely homogeneous systems.

Some years ago we reported the preparation and characterization of a number of complexes of the water-soluble ligand $[Ph_2PCH_2CH_2NMe_3]^+$ (amphos)

which, when coordinated to metal atoms and ions via the alkyldiphenylphosphine group, forms complexes soluble in polar solvents because of the dangling ionic tetraalkyl ammonium group [3]. Amphos complexes of rhodium(I) exhibit interesting properties as biphasic catalysts, either in aqueous–organic solvent systems or tethered to a cation exchange resin via the phosphonium group [3c]. More recently, we extended this work to the new class of water-soluble phosphines $[Ph_2P(CH_2)_n\text{-}PMe_3]^+$ ("*n*-phophos": n = 2, 3, 6 and 10, henceforth denoted II-, III-, VI- and X-phophos respectively), designed to make possible an investigation of the effects of chain length on the catalytic properties of the corresponding rhodium(I) complexes. As anticipated, the increased chain length does indeed result in an increase in hydrogenation activity of the catalysts towards olefins in both aqueous–organic biphasic systems or when tethered to a cation exchange resin via the phosphonium groups [2j].

The observed trends suggested greater catalyst site accessibility and hence perhaps mobility for complexes of the longer-chain ligands. Since differences in molecular mobility might also be reflected in the ^{31}P spin–lattice relaxation times T_1, we initiated in an investigation of the ^{31}P NMR behaviour of the phophos ligands [4], but could not study the rhodium complexes because of the close similarities of the pairs of phosphonium and

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coordinated phosphine ^{31}P chemical shifts. In order therefore to extend this investigation, we have prepared two series of phophos–iron complexes of the types [Fe(CO)$_4$(n-phophos)]$^+$ and [CpFe(CO)$_2$(n-phophos)]$^{2+}$ (n = 2, 3, 6 and 10), chosen in part in order to be able to obtain comparative complexes in which the metal centres are neutral and cationic; the latter may also interact with a cation exchange resin. As the first stage of this work, we now report the syntheses and characterization of the two new series of compounds and provide limited data for the bis-phophos complexes *trans*-[Fe(CO)$_3$(n-phophos)$_2$]$^{2+}$, which occur as minor components in mixtures with their monosubstituted counterparts.

2. Experimental section

All manipulations were carried out under purified nitrogen by using standard Schlenk techniques and a Vacuum Atmospheres glove-box. All solvents were freshly distilled under nitrogen. Deuterated solvents were purchased from Isotec Inc. and degassed and stored in the glove-box. The phophos ligands [Ph$_2$P(CH$_2$)$_n$ PMe$_3$]X (n = 2, 3, 6, 10; X = NO$_3$, Cl, PF$_6$) were synthesized according to literature methods [2j] and the iron compounds Fe$_2$(CO)$_9$ (Strem) and [CpFe(CO)$_2$]$_2$ (Aldrich) were used as received. Solution IR spectra were recorded on a Bruker IFS-25 Fourier transform IR spectrometer using a 0.2 mm NaCl cell. NMR spectra were acquired on Bruker AC-200 (200.1 MHz, ^{1}H) and AM-400 (400.2 MHz, ^{1}H, 100.6 MHz, ^{13}C{^{1}H}; 162.0 MHz, ^{31}P{^{1}H}) NMR spectrometers. Fast atom bombardment (FAB)(+) mass spectra were obtained on a

Fisons VG Quattro triple quadrupole mass spectrometer. The salts were dissolved in a minimum amount of acetone and 2% acetic acid in 3-nitrobenzyl alcohol was added for the matrix. Elemental analyses were carried out by Canadian Microanalytical Services Ltd. (Delta, B.C.).

2.1. General procedures for syntheses of the complexes [Fe(CO)$_4$(n-phophos)]X and trans-[Fe(CO)$_3$(n-phophos)$_2$]X$_2$ (n = 2, 3, 6 and 10; X = NO$_3$, Cl, PF$_6$ or BPh$_4$)

Typically 0.36 g (1.0 mmol) of Fe$_2$(CO)$_9$ and 1.0 mmol of [Ph$_2$PCH$_2$CH$_2$PMe$_3$]NO$_3$ (II-phophos nitrate) (0.35 g), [Ph$_2$PCH$_2$CH$_2$PMe$_3$]PF$_6$ (II-phophos hexafluorophosphate) (0.43 g), [Ph$_2$P(CH$_2$)$_3$PMe$_3$]Cl (III-phophos chloride) (0.34 g), [Ph$_2$P(CH$_2$)$_6$PMe$_3$]PF$_6$ (VI-phophos hexafluorophosphate) (0.49 g) or [Ph$_2$P (CH$_2$)$_{10}$PMe$_3$]NO$_3$ (X-phophos nitrate) (0.46 g) were reacted in 50 ml of tetrahydrofuran (THF). The originally yellow–orange solutions containing undissolved Fe$_2$(CO)$_9$ changed colour to brown upon stirring for about 15 min at room temperature and became homogeneous. Stirring was continued for an additional hour and IR analysis of a solution sample at this point showed the presence of Fe(CO)$_5$, Fe(CO)$_4$L and some *trans*-Fe(CO)$_3$L$_2$ (L = n-phophos). The solvent and Fe(CO)$_5$ were then removed under vacuum to give yellow-brown oils which were washed with ether and hexane and dried in vacuum overnight resulting in the formation of yellow air-stable foam-like solids. Usually, these solids were mixtures of monosubstituted and disubstituted derivatives except for [Fe(CO)$_4$(II-phophos)]NO$_3$, which was obtained as the sole product.

Table 1
FAB(+) mass spectroscopy data for iron carbonyl complexes containing the phophos ligands [PPh$_2$(CH$_2$)$_n$PMe$_3$]X(n = 2, 3, 6 and 10)

Compound	Major positive ions (m/z)
[Fe(CO)$_4$(II-phophos)]NO$_3$	[M]$^+$ (457, 82%), [M-CO]$^+$ (429, 2%), [M-2CO]$^+$ (401, 7%), [M-3CO]$^+$ (373, 13%), [M-4CO]$^+$ (345, 16%), [O=PPh$_2$CH$_2$CH$_2$PMe$_3$]$^+$ (305, 8%), [Ph$_2$PCH$_2$CH$_2$PMe$_3$]$^+$ (289, 100%)
[Fe(CO)$_4$(II-phophos)]PF$_6$	[M]$^+$ (457, 37%), [M-CO]$^+$ (429, 1%), [M-2CO]$^+$ (401, 6%), [M-3CO]$^+$ (373, 13%), [M-4CO]$^+$ (345, 18%), [O=PPh$_2$CH$_2$CH$_2$PMe$_3$]$^+$ (305, 9%), [Ph$_2$PCH$_2$CH$_2$PMe$_3$]$^+$ (289, 100%)
[Fe(CO)$_3$(II-phophos)$_2$](PF$_6$)$_2$	[MPF$_6$]$^+$(863, 6%)
[Fe(CO)$_4$(III-phophos)]BPh$_4$	[M]$^+$ (471, 100%), [M-CO]$^+$ (443, 8%), [M-2CO]$^+$ (415, 6%), [M-3CO]$^+$ (387, 12%), [M-4CO]$^+$ (358, 13%), [O=PPh$_2$(CH$_2$)$_3$PMe$_3$]$^+$ (319, 45%), [Ph$_2$P(CH$_2$)$_3$PMe$_3$]$^+$ (303, 85%)
[Fe(CO)$_3$(III-phophos)$_2$](BPh$_4$)$_2$	[MBPh$_4$]$^+$ (1066, 1%)
[Fe(CO)$_4$(VI-phophos)]PF$_6$	[M]$^+$ (513, 25%), [M-CO]$^+$ (485, 3%), [M-2CO]$^+$ (457, 15%), [M-3CO]$^+$ (429, 8%), [M-4CO]$^+$ (401, 5%), [O=PPh$_2$(CH$_2$)$_6$PMe$_3$]$^+$ (361, 14%), [Ph$_2$P(CH$_2$)$_6$PMe$_3$]$^+$ (345, 100%)
[Fe(CO)$_3$(VI-phophos)$_2$](PF$_6$)$_2$	[MPF$_6$]$^+$ (975, 2%)
[Fe(CO)$_4$(X-phophos)]BPh$_4$	[M]$^+$ (569, 7%), [M-CO]$^+$ (541, 3%) [M-2CO]$^+$ (513, 11%), [M-3CO]$^+$ (485, 4%), [M-4CO]$^+$ (457, 6%), [O=PPh$_2$(CH$_2$)$_{10}$PMe$_3$]$^+$ (418, 36%), [Ph$_2$P(CH$_2$)$_{10}$PMe$_3$]$^+$ (402, 100%)
[Fe(CO)$_3$(X-phophos)$_2$](BPh$_4$)$_2$	[MBPh$_4$]$^+$ (1262, 2%)
[CpFe(CO)$_2$(II-phophos)](NO$_3$)(PF$_6$)	[MPF$_6$]$^+$ (611, 16%), [MNO$_3$]$^+$ (528, 2%), [O=PPh$_2$CH$_2$CH$_2$PMe$_3$]$^+$ (305, 16%), [Ph$_2$PCH$_2$CH$_2$PMe$_3$]$^+$ (289, 100%)
[CpFe(CO)$_2$(III-phophos)]Cl(PF$_6$)	[MPF$_6$]$^+$ (625, 7%), [MCl]$^+$ (517 and 515, 4 and 11% respectively), [O=PPh$_2$(CH$_2$)$_3$PMe$_3$]$^+$ (319, 38%), [Ph$_2$P(CH$_2$)$_3$PMe$_3$]$^+$ (303, 100%)
[CpFe(CO)$_2$(VI-phophos)](PF$_6$)$_2$	[MPF$_6$]$^+$ (667, 49%), [O=PPh$_2$(CH$_2$)$_6$PMe$_3$]$^+$ (361, 13%), [Ph$_2$P(CH$_2$)$_6$PMe$_3$]$^+$ (345, 100%)
[CpFe(CO)$_2$(X-phophos)](BPh$_4$)$_2$	[MBPh$_4$]$^+$ (897, 7%), [O=PPh$_2$(CH$_2$)$_{10}$PMe$_3$]$^+$ (418, 11%), [Ph$_2$P(CH$_2$)$_{10}$PMe$_3$]$^+$ (402, 100%)

These phophos-substituted iron(0) complexes were, however, difficult to obtain free of solvent and hence analytically pure. Further purification was carried out by dissolving the crude materials in 5 ml of acetone and precipitating the oils with ether. The mother liquors were decanted and, after the remaining oils were washed with copious amonts of ether and hexane, they were dried in vacuum overnight. In this way, the II-phophos complex [Fe(CO)$_4$(II-phophos)]NO$_3$ was obtained analytically pure and the VI-phophos analogue was obtained as a 1:0.3 molar mixture of [Fe(CO)$_4$(VI-phophos)]PF$_6$ and [Fe(CO)$_3$(VI-phophos)$_2$](PF$_6$)$_2$ (see analytical data below).

However, this procedure was not sufficient for the III- and X-phophos-substituted chloride and nitrate complexes, which were found to be more difficult to free of solvent. The purities of the originally isolated mixtures of [Fe(CO)$_4$(n-phophos)]X and [Fe(CO)$_3$(n-phophos)$_2$]X$_2$ (n = 3; X = Cl) (n = 10; X = NO$_3$) were improved by converting them into the less soluble BPh$_4^-$ salts. To this end, the crude materials were dissolved in 5 ml of CH$_2$Cl$_2$ and treated with 2 ml of MeOH solution containing 0.34 g (1.0 mmol) NaBPh$_4$. The cloudy solutions were filtered through Celite and evaporated to dryness in vacuo, and the resulting solids were washed several times with 10 ml portions of ether and dried overnight in vacuum to give light-yellow powders. Yields and analytical ^{1}H NMR and ^{13}C{^{1}H} NMR data for the products are listed below. FAB(+) mass spectroscopy, IR spectroscopy and ^{31}P{^{1}H} NMR spectroscopy data appear in Tables 1, 2 and 3 respectively.

2.1.1. [Fe(CO)$_4$(II-phophos)]NO$_3$

This was prepared from the reaction of Fe$_2$(CO)$_9$ with II-phophos nitrate (yield, 0.35 g, 0.67 mmol (67%)). Anal. Found: C, 48.11; H, 4.41. C$_{21}$H$_{23}$FeNO$_7$P$_2$ Calc.: C, 48.58; H, 4.47%. ^{1}H NMR (acetone-d_6): δ 2.20 (d, J_{PH} = 14.8 Hz, 9H, Me), 2.77 (m, 2H, CH$_2$), 3.10 (m,

Table 2
IR data in the carbonyl stretching region

Compound	ν(CO) (cm^{-1}) [a]
[Fe(CO)$_4$(II-phophos)]NO$_3$	2053 (s), 1980 (m), 1945 (vs), 1929 (vs)
[Fe(CO)$_4$(II-phophos)]PF$_6$	2054 (vs), 1982 (m), 1946 (vs), 1929 (vs)
[Fe(CO)$_4$(III-phophos)]Cl	2049 (m), 1976 (w), 1937 (vs), 1930 (vs, sh)
[Fe(CO)$_4$(III-phophos)]BPh$_4$	2048 (s), 1973 (m), 1941 (vs, sh), 1931 (vs) [b]
[Fe(CO)$_4$(VI-phophos)]PF$_6$	2047 (m), 1971 (w), 1935 (vs, br)
[Fe(CO)$_4$(X-phophos)]NO$_3$	2047 (w-m), 1971 (w), 1935 (vs)
[Fe(CO)$_4$(X-phophos)]BPh$_4$	2046 (s), 1968 (m), 1932 (vs, br) [b]
[Fe(CO)$_3$(II-phophos)$_2$](PF$_6$)$_2$	1984, 1881
[Fe(CO)$_3$(III-phophos)$_2$](BPh$_4$)$_2$	1885, 1871 [b]
[Fe(CO)$_3$(VI-phophos)$_2$](PF$_6$)$_2$	1881, 1867
[Fe(CO)$_3$(X-phophos)$_2$](BPh$_4$)$_2$	1883, 1872 [b]
[CpFe(CO)$_2$(II-phophos)](NO$_3$)(PF$_6$)	2065 (vs), 2056 (sh), 2019 (vs), 2000 (sh)
[CpFe(CO)$_2$(III-phophos)]Cl(PF$_6$)	2052 (vs), 2007 (vs)
[CpFe(CO)$_2$(VI-phophos)](PF$_6$)$_2$	2054 (vs), 2010 (vs)
[CpFe(CO)$_2$(X-phophos)](NO$_3$)(PF$_6$)	2053 (vs), 2009 (vs)
[CpFe(CO)$_2$(X-phophos)](BPh$_4$)$_2$	2053 (vs), 2010 (vs)

[a] In CH$_2$Cl$_2$ unless noted otherwise.
[b] In THF.

2H, CH$_2$), 7.58 (m, 6H, m,p-Ph), 7.70 (m, 4H, o-Ph) ppm. ^{13}C{^{1}H} NMR (CD$_3$CN): δ 7.9 (d, J_{PC} = 54.3 Hz, Me), 19.7 (d, J_{PC} = 51.3 Hz, CH$_2$), 25.1 (dd, $J_{PC(1)}$ = 28.8 Hz, $J_{PC(2)}$ ≈ 4 Hz, CH$_2$), 130.2 (d, J_{PC} = 10.2 Hz, m-Ph), 132.6 (s, br, p-Ph), 133.1 (d, J_{PC} = 9.9 Hz, o-Ph), 133.5 (d, J_{PC} ≈ 48 Hz, $ipso$-Ph, slight overlap with o-Ph), 214.1 (d, J_{PC} = 18.8 Hz, CO) ppm.

2.1.2. [Fe(CO)$_4$(II-phophos)]PF$_6$

This was prepared from the reaction of Fe$_2$(CO)$_9$ with II-phophos hexafluorophosphate and obtained as a

Table 3
^{31}P{^{1}H} NMR data

Compound	δ [a] (ppm)	
	PPh$_2$	PMe$_3$
[Fe(CO)$_4$(II-phophos)]NO$_3$	71.3 (d, $^3J_{PP}$ = 54 Hz)	33.2 (d, $^3J_{PP}$ = 54 Hz)
[Fe(CO)$_4$(II-phophos)]PF$_6$	71.5 (d, $^3J_{PP}$ = 54 Hz)	32.7 (d, $^3J_{PP}$ = 54 Hz)
[Fe(CO)$_3$(II-phophos)$_2$](PF$_6$)$_2$	79.9 (m)	32.3 (m)
[Fe(CO)$_4$(III-phophos)]BPh$_4$	66.0 (d, $^4J_{PP}$ = 4.9 Hz)	28.7 (d, $^4J_{PP}$ = 4.9 Hz)
[Fe(CO)$_3$(III-phophos)$_2$](BPh$_4$)$_2$	75.7 (s)	28.7 (s)
[Fe(CO)$_4$(VI-phophos)]PF$_6$	65.3 (s)	29.1 (s)
[Fe(CO)$_3$(VI-phophos)$_2$](PF$_6$)$_2$	75.3 (s)	29.1 (s)
[Fe(CO)$_4$(X-phophos)]BPh$_4$	65.2 (s)	28.9 (s)
[Fe(CO)$_3$(X-phophos)$_2$](BPh$_4$)$_2$	75.4 (s)	28.8 (s)
[CpFe(CO)$_2$(II-phophos)](NO$_3$)(PF$_6$)	64.3 (d, $^3J_{PP}$ = 49 Hz)	33.7 (d, $^3J_{PP}$ = 49 Hz)
[CpFe(CO)$_2$(III-phophos)](BPh$_4$)$_2$	59.7 (d, $^4J_{PP}$ = 3.9 Hz)	28.7 (d, $^4J_{PP}$ = 4.8 Hz)
[CpFe(CO)$_2$(VI-phophos)](PF$_6$)$_2$	59.5 (s)	29.0 (s)
[CpFe(CO)$_2$(X-phophos)](BPh$_4$)$_2$	59.6 (s)	28.8 (s)

[a] Recorded in acetone-d_6 solutions relative to 85% H$_3$PO$_4$.

1 : 0.30 molar mixture (^{31}P NMR) with *trans*-[Fe(CO)$_3$(II-phophos)$_2$](PF$_6$)$_2$ (yield of the mixture, 0.48 g). ^{1}H NMR (acetone-d_6): δ 2.19 (d, $J_{PH} = 14.7$ Hz, 9H, Me), 2.77 (m, 2H, CH$_2$), 3.12 (m, 2H, CH$_2$), 7.61 (m, 6H, *m,p*-Ph), 7.77 (m, 4H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (CD$_3$CN): δ 8.0 (d, $J_{PC} = 54.5$ Hz, Me), 19.7 (d, $J_{PC} = 51.6$ Hz, CH$_2$), 25.0 (d, $J_{PC} = 29.3$ Hz, CH$_2$), 130.2 (d, $J_{PC} = 8.8$ Hz, *m*-Ph), 132.6 (s, *p*-Ph), 133.1 (d, $J_{PC} = 8.4$ Hz, *o*-Ph), ≈ 133 (d, *ipso*-Ph, partial overlap with *o*-Ph), 214.0 (d, $J_{PC} = 19.2$ Hz, CO) ppm.

2.1.3. trans-[Fe(CO)$_3$(II-phophos)$_2$](PF$_6$)$_2$

^{1}H NMR data are identical with those of [Fe(CO)$_4$(II-phophos)]PF$_6$. ^{13}C{^{1}H} NMR (CD$_3$CN): δ 8.1 (d, $J_{PC} = 55.0$ Hz, Me), 19.9 (d, $J_{PC} = 51.8$ Hz, CH$_2$), 25.0 (d, $J_{PC} = 28.8$ Hz, CH$_2$), 129.8 (d, $J_{PC} \approx 6$ Hz, *m*-Ph), 131.9 (s, *p*-Ph) ppm; other resonances were not observed, probably because of overlap with those of [Fe(CO)$_4$(II-phophos)]PF$_6$.

2.1.4. [Fe(CO)$_4$(III-phophos)]BPh$_4$

This was obtained after metathesis with NaBPh$_4$ as a 1 : 0.04 molar mixture (^{31}P NMR) with *trans*-[Fe(CO)$_3$(III-phophos)$_2$](BPh$_4$)$_2$ (yield of the mixture, 0.39 g). Anal. Found: C, 72.33; H, 5.72. Mixture of C$_{46}$H$_{45}$BFeO$_4$P$_2$ containing 4% C$_{87}$H$_{90}$B$_2$FeO$_3$P$_4$ Calc.: C, 70.26; H, 5.79% ^{1}H NMR (acetone-d_6): δ 1.90 (d, $J_{PH} = 14.4$ Hz, 9H, Me), 2.00 (m, 2H, CH$_2$), 2.54 (m, 2H, CH$_2$), 2.83 (m, 2H, CH$_2$), 6.76 ("t", 4H, BPh), 6.92 ("t", 8H, BPh), 7.33 (m, 8H, BPh), 7.57 (m, 6H, *m,p*-Ph), 7.67 (m, 4H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (CD$_3$CN): δ 8.1 (d, $J_{PC} = 54.8$ Hz, Me), 17.9 (s, CH$_2$), 24.6 (dd, $J_{PC(1)} = 51.6$ Hz, $J_{PC(2)} = 16.3$ Hz, CH$_2$), 33.9 (dd, $J_{PC(1)} = 30.2$ Hz, $J_{PC(2)} = 17.3$ Hz, CH$_2$), 122.8 (s, *p*-BPh), 126.6 (s, *m*-BPh), 130.0 (d, $J_{PC} = 8.6$ Hz, *m*-PPh), 132.3 (s, *p*-PPh), 133.0 (d, $J_{PC} = 9.2$ Hz, *o*-PPh), 134.3 (d, $J_{PC} = 47.8$ Hz, *ipso*-PPh), 136.7 (s, *o*-BPh), 164.8 (q, $J = 49.3$ Hz, *ipso*-BPh), 214.4 (d, $J_{PC} = 19.2$ Hz, CO) ppm.

2.1.5. trans-[Fe(CO)$_3$(III-phophos)$_2$](BPh$_4$)$_2$

^{1}H NMR (acetone-d_6): δ 1.76 (d, $J_{PH} = 14.5$ Hz, Me) ppm; because of the relatively low proportion of this complex in the mixture, other resonances were not observed.

2.1.6. [Fe(CO)$_4$(VI-phophos)]PF$_6$

This was obtained as a 1 : 0.3 molar mixture (^{31}P NMR) with *trans*-[Fe(CO)$_3$(VI-phophos)$_2$](PF$_6$)$_2$ (yield of the mixture, 0.53 g). Anal. Found: C, 46.30, H, 5.04. 1:0.3 mixture of C$_{25}$H$_{31}$F$_6$FeO$_4$P$_3$ and C$_{45}$H$_{62}$F$_{12}$-FeO$_3$P$_6$ Calc.: C, 46.51; H, 5.03%. ^{1}H NMR (acetone-d_6): δ 1.58–1.70 (m, br, 8H, CH$_2$), 2.03 (d, $J_{PH} = 14.6$ Hz, 9H, Me), 2.37 (m, 2H, CH$_2$), 2.65 (m, 2H, CH$_2$), 7.57 (m, 6H, *m,p*-Ph), 7.68 (m, 4H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (CD$_3$CN): δ 8.2 (d, $J_{PC} = 55.1$ Hz, Me), 21.6 (d,

$J_{PC} = 3.6$ Hz, CH$_2$), 23.6 (d, $J_{PC} = 52.6$ Hz, CH$_2$), 24.8 (s, CH$_2$), 30.3 (dd, $J_{PC(1)} = 15.1$ Hz, $J_{PC(2)} = 10.4$ Hz, CH$_2$), 32.9 (d, $J_{PC} = 31.5$ Hz, CH$_2$), 129.8 (d, $J_{PC} = 9.4$ Hz, *m*-Ph), 132.0 (s, *p*-Ph), 132.9 (d, $J_{PC} = 10.6$ Hz, *o*-Ph), 135.1 (d, $J_{PC} = 47.6$ Hz, *ipso*-Ph), 214.7 (d, $J_{PC} = 19.2$ Hz, CO) ppm.

2.1.7. trans-[Fe(CO)$_3$(VI-phophos)$_2$](PF$_6$)$_2$

^{1}H NMR (acetone-d_6): δ 1.99 (d, $J_{PH} = 14.5$ Hz, Me), 7.48–7.61 (m, Ph) ppm; all other resonances are identical to those of [Fe(CO)$_4$(VI-phophos)]PF$_6$. ^{13}C{^{1}H} NMR (CD$_3$CN): δ 25.0 (s, CH$_2$), 129.4 (s, br, *m*-Ph), 131.1 (s, *p*-Ph), 137.9 (d, $J_{PC} = 44.1$ Hz, *ipso*-Ph), 215.5 (t, $J_{PC} = 28.8$ Hz, CO) ppm; all other resonances overlap with those of [Fe(CO)$_4$(VI-phophos)]PF$_6$.

2.1.8. [Fe(CO)$_4$(X-phophos)]BPh$_4$

This was obtained after metathesis with NaBPh$_4$ as a 1 : 0.75 molar mixture (^{31}P NMR) with *trans*-[Fe(CO)$_3$(X-phophos)$_2$](BPh$_4$)$_2$ (yield of the mixture, 0.60 g). Anal. Found: C, 74.21; H, 7.23. 1 : 0.75 mixture of C$_{53}$H$_{59}$BFeO$_4$P$_2$ and C$_{101}$H$_{118}$B$_2$FeO$_3$P$_4$ Calc.: C, 74.57; H, 7.17%. ^{1}H NMR (acetone-d_6): δ 1.43–1.62 (m, 16H, CH$_2$), 1.90 (d, $J_{PH} = 14.5$ Hz, 9H, Me), 2.21 (m, 2H, CH$_2$), 2.61 (m, 2H, CH$_2$), 6.78 ("t", 4H, BPh), 6.93 ("t", 8H, BPh), 7.34 (m, 8H, BPh), 7.55 (m, 6H, *m,p*-PPh), 7.71 (m, 4H, *o*-PPh) ppm. ^{13}C{^{1}H} NMR (CD$_3$CN): δ 8.2 (d, $J_{PC} = 54.7$ Hz, Me), 21.8 (d, $J_{PC} = 3.6$ Hz, CH$_2$), 23.7 (d, $J_{PC} = 52.4$ Hz, CH$_2$), 25.1 (d, $J_{PC} = 20.2$ Hz, CH$_2$), 29.4 (s, CH$_2$), 29.7 (s, CH$_2$), 29.8 (s, CH$_2$), 31.0 (d, $J_{PC} = 16.0$ Hz, CH$_2$), 33.1 (d, $J_{PC} = 30.7$ Hz, CH$_2$), 122.8 (s, *p*-BPh), 126.6 (s, *m*-BPh), 129.8 (d, $J_{PC} = 9.9$ Hz, *m*-PPh), 132.0 (s, *p*-PPh), 132.9 (d, $J_{PC} \approx 8$ Hz, *o*-PPh), 135.2 (d, $J_{PC} = 47.3$ Hz, *ipso*-PPh), 136.7 (s, *o*-BPh), 164.8 (q, $J = 49.2$ Hz, *ipso*-BPh), 214.7 (d, $J_{PC} = 19.4$ Hz, CO) ppm.

2.1.9. trans-[Fe(CO)$_3$(X-phophos)$_2$](BPh$_4$)$_2$

^{1}H NMR (acetone-d_6): δ 1.85 (d, $J_{PH} = 14.4$ Hz, Me) ppm; all other resonances are identical with those of [Fe(CO)$_4$(X-phophos)]BPh$_4$. ^{13}C{^{1}H} NMR (CD$_3$CN): δ 29.5 (s, CH$_2$), 29.8 (s, CH$_2$), 29.9 (s, CH$_2$), 31.2 (d, $J_{PC} = 15.0$ Hz, CH$_2$), 33.9 (d, $J_{PC} = 30.8$ Hz, CH$_2$), 129.4 (s, br, *m*-PPh), 131.0 (s, *p*-PPh), 138.1 (d, $J_{PC} = 43.8$ Hz, *ipso*-PPh), 215.6 (t, $J_{PC} = 28.4$ Hz, CO) ppm; all other resonances are identical to those of [Fe(CO)$_4$(X-phophos)]BPh$_4$.

2.2. General procedures for syntheses of the complexes [CpFe(CO)$_2$(n-phophos)]X$_2$ (n = 2, 3, 6 and 10; X = NO$_3$, Cl, PF$_6$ or BPh$_4$)

These complexes were prepared by the method of Schumann [5]. In a typical procedure, 0.18 g (0.5 mmol) of [CpFe(CO)$_2$]$_2$, 0.33 g (1.0 mmol) of [Cp$_2$Fe]PF$_6$ and 1.0 mmol of the corresponding phophos ligand were

dissolved in 20 ml of CH_2Cl_2 and stirred at room temperature. The greenish-blue color of the initial solutions changed to orange in about 15 min, and IR spectra taken after about 1 h indicated complete consumption of $[CpFe(CO)_2]_2$ and formation of the expected complexes as sole products. The reaction mixtures were evaporated to dryness and the solid residues were washed with several 10 ml portions of ether to remove ferrocene. The greenish-yellow solids were then washed with hexane and dried in vacuo; in some cases, metathesis reactions were carried out with $NaBPh_4$ in CH_2Cl_2–MeOH as for the iron(0) complexes. The products were characterized by FAB(+) MS (Table 1), and IR (Table 2), ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR (Table 3) spectroscopy.

2.2.1. [CpFe(CO)₂(II-phophos)](NO₃)(PF₆)

Yield, 0.62 g (92%). Anal. Found: C, 43.09; H, 4.34%. $C_{24}H_{28}F_6FeNO_5P_3$ Calc.: C, 42.82; H, 4.19. ^1H NMR (acetone-d_6): δ 2.15 (d, $J_{PH} = 14.8$ Hz, 9H, Me), 2.71 (m, 2H, CH_2), 3.55 (m, 2H, CH_2), 5.72 (d, $J_{PH} = 1.5$ Hz, 5H, Cp), 7.66 (m, 10H, Ph) ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 7.6 (d, $J_{PC} = 54.2$ Hz, Me), 19.4 (d, $J_{PC} = 51.4$ Hz, CH_2), 25.0 (d, $J_{PC} = 26.4$ Hz, CH_2), 89.8 (s, Cp), 130.6 (s, br, *m*-Ph), 131.9 (d, $J_{PC} = 53.6$ Hz, *ipso*-Ph), 133.1 (s, br, *o,p*-Ph), 210.5 (d, $J_{PC} = 23.7$ Hz, CO) ppm.

2.2.2. [CpFe(CO)₂(III-phophos)]Cl(PF₆)

Yield: 0.57 g (86%). Anal. Found: C, 43.29; H, 4.58. $C_{25}H_{30}ClF_6FeO_2P_3$ Calc.: C, 45.45; H, 4.58%. ^1H NMR of the BPh_4^- salt (acetone-d_6): δ 1.71 (d, $J_{PH} = 15.0$ Hz, 9H, Me), 2.15 (m, 2H, CH_2), 2.79 (m, 2H, CH_2), 3.27 (m, 2H, CH_2), 5.41 (s, 5H, Cp), 6.76 ("t", 8H, BPh), 6.91 ("t", 16H, BPh), 7.32 (m, 16H, BPh), 7.63 (m, 10H, PPh) ppm. $^{13}C\{^1H\}$ NMR (CD₃CN): δ 18.3 (d, $J_{PC} = 54.4$ Hz, Me), 19.6 (s, CH_2), 24.0 (m, CH_2), 40.6 (m, CH_2), 93.5 (s, Cp), 130.8 (d, $J_{PC} = 8.5$ Hz, *m*-Ph), 132.2 (d, $J_{PC} = 51.3$ Hz, *ipso*-Ph), 132.9 (s, *p*-Ph), 135.7 (d, $J_{PC} = 8.6$ Hz, *o*-Ph), 210.8 (d, $J_{PC} = 24.0$ Hz, CO) ppm.

2.2.3. [CpFe(CO)₂(VI-phophos)](PF₆)₂

Yield: 0.72 g (89%). Anal. Found: C, 41.11; H, 4.38. $C_{28}H_{36}F_{12}FeO_2P_4$ Calc.: C, 41.40; H, 4.47%. ^1H NMR (acetone-d_6): δ 1.50–1.64 (m, 8H, CH_2), 1.98 (d, $J_{PH} = 14.5$ Hz, 9H, Me), 2.31 (m, 2H, CH_2), 2.86 (m, 2H, CH_2), 5.54 (d, $J_{PH} = 1.6$ Hz, 5H, Cp), 7.65 (m, 10H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD₃CN): δ 8.1 (d, $J_{PC} = 54.7$ Hz, Me), 21.6 (d, $J_{PC} = 3.9$ Hz, CH_2), 23.5 (d, $J_{PC} = 52.4$ Hz, CH_2), 24.5 (s, CH_2), 30.2 (d, $J_{PC} = 15.6$ Hz, CH_2), 32.8 (d, $J_{PC} = 31.9$ Hz, CH_2), 89.4 (s, Cp), 130.5 (s, br, *m*-Ph), 132.4 (d, $J_{PC} = 50.6$ Hz, *ipso*-Ph), 133.0 (s, *o,p*-Ph), 210.9 (d, $J_{PC} = 23.7$ Hz, CO) ppm.

2.2.4. [CpFe(CO)₂(X-phophos)](BPh₄)₂

Yield, 0.99 g (82%). ^1H NMR (acetone-d_6): δ 1.22–1.40 (m, 14H, CH_2), 1.61 (m, 2H, CH_2), 1.92 (d, $J_{PH} = 14.6$ Hz, 9H, Me), 2.25 (m, 2H, CH_2), 2.82 (m, 2H, CH_2), 5.43 (d, $J_{PH} = 1.5$ Hz, 5H, Cp), 6.76 ("t", 8H, BPh), 6.91 ("t", 16H, BPh), 7.33 (m, 16H, BPh), 7.62 (m, 10H, PPh) ppm. $^{13}C\{^1H\}$ NMR (CD₃CN): δ 8.2 (d, $J_{PC} = 55.2$ Hz, Me), 21.8 (s, CH_2), 23.7 (d, $J_{PC} = 52.3$ Hz, CH_2), 24.8 (s, CH_2), 29.5 (s, CH_2), 29.9 (d, $J_{PC} = 5.8$ Hz, CH_2), 31.0 (d, $J_{PC} = 16.4$ Hz, CH_2), 33.0 (d, $J_{PC} = 30.5$ Hz, CH_2), 89.4 (s, Cp), 122.8 (s, *p*-BPh), 126.6 (s, *m*-BPh), 130.4 (d, $J_{PC} \approx 7$ Hz, *m*-PPh), 132.5 (d, $J_{PC} = 50.4$ Hz, *ipso*-PPh), 133.0 (s, *o,p*-PPh), 136.7 (s, *o*-BPh), 164.8 (q, $J = 49.6$ Hz, *ipso*-BPh), 211.0 (d, $J_{PC} = 24.1$ Hz, CO) ppm.

3. Results and discussion

3.1. Synthesis and characterization of complexes [Fe(CO)₄(n-phophos)]X and trans-[Fe(CO)₃(n-phophos)₂]X₂ (n = 2, 3, 6 and 10; X = NO₃, Cl, PF₆ or BPh₄)

These series of compounds containing the phophos ligands coordinated to neutral iron(0) centres were readily obtained by reacting equimolar amounts of $Fe_2(CO)_9$ with the phosphines in THF at room temperature. In general, the substitutions led to the product mixture shown in the following equation:

$$Fe_2(CO)_9 + L \rightarrow Fe(CO)_5 + Fe(CO)_4L$$
$$+ \textit{trans}\text{-}Fe(CO)_3L_2 \qquad (1)$$
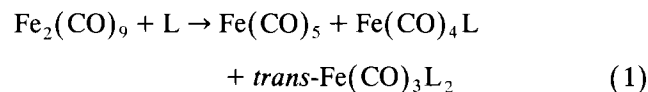
as has been observed with the analogous reactions of neutral tertiary phosphines [6]. Using $Fe_2(CO)_9$ in excess (10–20%) did not substantially change the amounts of disubstituted byproducts. From the reaction mixtures, the substituted complexes were isolated as yellow amorphous solids. The minor amounts of disubstituted derivatives were not separated from the major monosubstituted compounds but could readily be identified and characterized spectroscopically. The two series of compounds represent the first zero-oxidation-state transition metal carbonyl complexes substituted with phophos ligands.

In the course of our search for more suitable synthetic methods, direct thermal [7], $[CpFe(CO)_2]_2$-catalyzed [8] and Me_3NO-assisted [9] substitutions of $Fe(CO)_5$ with the phophos ligands, widely utilized previously for the preparation of monosubstituted and disubstituted derivatives containing a variety of tertiary phosphines, were attempted but with no general success. In most cases, either no reaction occurred or unidentified decomposition products were obtained.

The identities of the monosubstituted complexes were confirmed in most cases by elemental analyses and were verified by FAB(+) mass spectroscopy (Table 1). Relatively high intensity peaks attributable to the molecular ions were present in each spectrum, as were peaks attributable to cations formed by stepwise loss of CO. The base peaks in most cases were those of the free cationic phophos ligands, formed by decomposition in the chamber of the spectrometer. High abundances of phosphonium molecular ions in the FAB mass spectra were also demonstrated by others [10]. The phophos ligand peaks were always accompanied by a much less intense peak appearing 16 m/z units higher, probably attributable to the corresponding phosphine oxides.

In contrast, peaks attributable to the dipositive molecular ions of the disubstituted complexes could not be observed and peaks attributable to ion-paired molecular ions of the type $[Fe(CO)_3(n\text{-phophos})_2X]^+$ ($[MX]^+$) were generally very weak even when these species were present in relatively high molar ratios in the product mixtures. In addition, there were observed no peaks attributable to products of loss of CO from either $[Fe(CO)_3(n\text{-phophos})_2]^{2+}$ or $[Fe(CO)_3(n\text{-phophos})_2X]^+$. On the other hand, the phophos ligands originating from these compounds might also greatly contribute to the high intensity of the free phophos peak in the spectra of product mixtures. In fact, the intensity ratios of the $[M]^+$: free phophos peaks in the spectra of samples containing little or no disubstituted byproducts were found to be much higher than in the others.

The IR spectra (Table 2) of the compounds are consistent with the structures suggested and are similar to those containing both neutral tertiary phosphines and amphos [3a,b]. A typical spectrum exhibits three bands ($2A_1 + E$), characteristic of trigonal bipyramidal $Fe(CO)_4L$ complexes of C_{3v} symmetry containing the substituent in axial position [11]. Although several examples are known where the E mode $v(CO)$ vibration is split [12], it is worth mentioning that the splitting of the E mode of the monosubstituted complexes decreases with increasing chain length. Thus well-resolved (about 17 and about 10 cm^{-1}) splitting was observed only for the II- and III-phophos complexes respectively, only a single, possibly slightly broadened absorbance appearing in the spectra of the other complexes. Also, the relatively short chain length in $[Fe(CO)_4(II\text{-phophos})]^+$ seems to result in decreased electron donation from the phosphine to iron, leading to a shift of the $v(CO)$ absorbances of this complex to somewhat higher frequencies relative to the others.

The disubstituted complexes were readily identified on the basis of characteristic IR absorbances appearing at lower wavenumbers than those of the monosubstituted complexes (Table 2), as with analogous compounds of neutral tertiary phosphines [6b,13]. The simple spectra consisting of a single band split into two
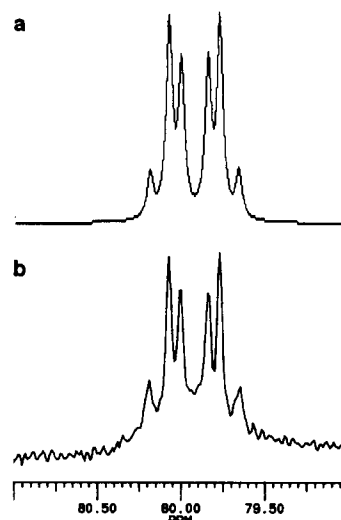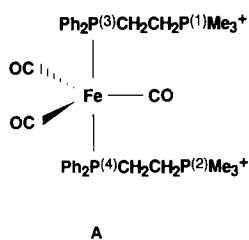

Fig. 1. (a) Simulated NMR spectrum of a four-spin XAA'X' system and (b) observed $^{31}P\{^1H\}$ NMR spectrum of *trans*-[Fe(CO)$_3$(II-phophos)$_2$](PF$_6$)$_2$ in the δ(PPh$_2$) region.

suggest bis-axial substituted bipyramidal structures of D_{3h} symmetry [11].

In accord with the IR spectra, the $^{31}P\{^1H\}$ NMR spectra are also very useful to distinguish the monosubstituted and disubstituted products (Table 3). Resonances for the latter complexes appear about 10 ppm downfield from those of the former, as has been reported for the analogous complexes of PMe$_2$Ph and PPh$_3$ [3b,13b,c].

As anticipated, phosphorus–phosphorus spin–spin coupling between the PPh$_2$ and PMe$_3^+$ groups cannot be observed for complexes of the longer-chain ligands. Interestingly, a four-bond coupling of about 5 Hz is observed in coordinated III-phophos, in contrast with the free ligand where no $^{31}P-^{31}P$ coupling was observed [2j]. The ^{31}P chemical shifts of the two types of phosphorus nucleus do not change with increase in chain length, and that of PPh$_2$ is essentially identical with that of coordinated amphos in [Fe(CO)$_4$(amphos)]I [3a,b]. The chemical shift of the non-coordinating PMe$_3^+$ moiety is relatively insensitive to the approximately 80 ppm change in δ(PPh$_2$) upon coordination.

However, the $^{31}P\{^1H\}$ NMR spectrum of *trans*-[Fe(CO)$_3$(II-phophos)$_2$](PF$_6$)$_2$ was found to be considerably different from the others. This particular spectrum exhibits not singlets, but identical multiplet resonances (Fig. 1(b)) for the tertiary and quaternary phosphorus nuclei, suggesting extensive $^{31}P-^{31}P$ coupling through the iron centre. Note that two-bond coupling constants of the phosphorus nuclei of neutral tertiary phosphines for some complexes of the type *trans*-Fe(CO)$_3$L$_2$ are known [14], but they typically do not appear because of obvious symmetry reasons. Thus, consistent with the relatively long range, four-bond coupling observed for [Fe(CO)$_4$(III-phophos)]BPh$_4$, a five-bond $^{31}P-^{31}P$ vir-

Ph$_2$P$^{(3)}$CH$_2$CH$_2$P$^{(1)}$Me$_3^+$

OC⁖,,
            |
         Fe —— CO
OC ⟋ |

Ph$_2$P$^{(4)}$CH$_2$CH$_2$P$^{(2)}$Me$_3^+$

A

tual coupling was apparent in the spectrum of *trans*-[Fe(CO)$_3$(II-phophos)$_2$](PF$_6$)$_2$. The corresponding four-spin XAA'X' system was simulated (Fig. 1(a)) and showed excellent correlation with the experimental spectrum (Fig. 1(b)) with the parameters J(P(1)P(3)) = J(P(2)P(4)) = 48 Hz, J(P(3)P(4)) = 30 Hz and J(P(1)P(4)) = J(P(2)P(3)) = 1 Hz (see A for assignments of the phosphorus nuclei). The P–Fe–P coupling is thus somewhat smaller (30 Hz) than reported for analogous complexes of neutral tertiary phosphines (about 60–100 Hz). To the best of our knowledge, *trans*-[Fe(CO)$_3$(II-phophos)$_2$](PF$_6$)$_2$ represents the first example where such a virtual coupling of phosphorus nuclei, arranged formally in an XAA'X' spin system, could be observed in a bis-tertiary phosphine complex.

The ^{13}C{^{1}H} and ^{1}H NMR resonances are considerably more sensitive to changes about both phosphorus nuclei, at least for those groups which are in close proximity to phosphorus. In addition, these spectra are consistent with the formulations of the monosubstituted complexes and merit little discussion. The ^{13}C{^{1}H} resonances of the CO ligands in the complexes [Fe(CO)$_4$(*n*-phophos)]$^+$ appear as single doublets, suggesting fluxionality. Complete ^{13}C{^{1}H} NMR spectra of the disubstituted iron complexes were not observed because of their relative low concentrations and because many of their resonances apparently overlap with and thus are obscured by those of the major monosubstituted derivatives.

3.2. Synthesis and characterization of complexes [CpFe(CO)$_2$(n-phophos)]X$_2$ (n = 2, 3, 6 and 10; X = NO$_3$, Cl, PF$_6$ or BPh$_4$)

This series of phophos complexes, containing a cationic iron(II) centre, was readily synthesized utilizing the recently published method of Schumann [5]; the procedure involves oxidation of [CpFe(CO)$_2$]$_2$ by ferricinium ion in the presence of the appropriate phophos ligand:

$$[CpFe(CO)_2]_2 + 2[Cp_2Fe]PF_6 + 2(\textit{n-phophos})X$$

$$\rightarrow 2[CpFe(CO)_2L]X(PF_6) + 2Cp_2Fe \qquad (2)$$
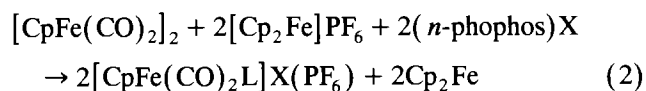
The products were obtained in excellent yields as green-ish-yellow solids and were characterized by elemental analyses and a variety of spectroscopic methods.

FAB(+) mass spectroscopy has been proven to be a highly useful technique for the analysis of the analogous complexes [CpRuP$_3$]$^+$ and [CpFe(CO)$_2$L]$^+$ (L = CO or olefin) [15], and we have found it equally convenient for the characterization of the cationic species [CpFe(CO)$_2$(*n*-phophos)]$^{2+}$. The ion-paired [MX]$^+$ peaks were readily recognizable as being the second most intense after those of the free phophos ligands (Table 1); two [MX]$^+$ peaks were observed when two different counteranions were present, but not peaks attributable to the [M]$^{2+}$ ions or ions arising from CO loss.

The IR spectra of the complexes generally exhibit two carbonyl stretching absorbances of equal intensity (Table 2), similar to spectra of analogous compounds of neutral tertiary phosphines [5]. As with the complexes of the type [Fe(CO)$_4$(*n*-phophos)]$^+$, the carbonyl stretching frequencies of the II-phophos complex are shifted to considerably higher frequencies, suggesting again a strong electronic effect of the relatively proximate PMe$_3^+$ moiety. In addition, both absorbances have strong shoulders arising from the presence of two rotamers about the Fe–P bond [16]. The ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra are consistent with the suggested structures and merit little further comment.

In continuing work, the temperature dependences of the T_1 values of the phosphine and phosphonium ^{31}P resonances are being measured for the two series of compounds, both in solution and tethered to a cation exchange resin. The results will be reported separately.

Acknowledgements

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