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Preparation and protonation reactions of aryl complexes of manganese and rhenium

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Abstract

Aryl $M(\kappa^1\text{-Ar})(CO)_nP_{5-n}$ [M = Mn, Re; Ar = C_6H_5, 4-$CH_3C_6H_4$; n = 2, 3; P = P(OEt)$_3$, PPh(OEt)$_2$, PPh$_2$OEt] and Re(κ^1-C_6H_5)(CO)$_3$[Ph$_2$PO(CH$_2$)$_3$OPPh$_2$] complexes were prepared by allowing hydrides MH(CO)$_n$P$_{5-n}$ to react first with triflic acid and then with the appropriate aryl lithium (LiAr) compounds. The complexes were characterized spectroscopically (IR and ^{1}H, ^{31}P, ^{13}C NMR) and by the X-ray crystal structure determination of Re(κ^1-C_6H_5)(CO)$_3$[Ph$_2$PO(CH$_2$)$_3$OPPh$_2$] derivative. Protonation reaction of the aryl complexes with HBF$_4 \cdot$ Et$_2$O lead to free hydrocarbons Ar–H and the unsaturated [M(CO)$_n$P$_{5-n}$]$^+$ cations, separated as solids in the case of [Re(CO)$_3$P$_2$]BF$_4$ derivatives.
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1. Introduction

Aryl complexes of transition metals are an important class of organometallic compounds which has been widely studied in the last forty years [1,2]. A number of metal complexes have been prepared using different methods, and the reactivity mode of both the coordinate aryl group and the metal fragment investigated.

However, an interesting but unexplored reaction of the aryl complexes [M]–Ar (Ar = Ph, *p*-tolyl) may be the protonation with Brønsted acid, which may involve the coordinate aryl group giving the aromatic hydrocarbons. The formation of the arene molecule in the coordination sphere of the metal may favour its η^2-coordination [3,4] on the metal center giving the corresponding derivatives. Complexes containing an η^2-arene ligand are known, and are generally prepared by reducing appropriate complexes in the presence of hydrocarbons [3,4]. Protonation of a σ-bonded κ^1-aryl complex may

be an alternative synthetic method, which finds a support in the parallel reaction of metal hydride with Brønsted acid to prepare η^2-H$_2$ dihydrogen derivatives [5,6].

We are interested in the synthesis and protonation of transition metal hydrides to obtain η^2-H$_2$ dihydrogen complexes and have reported several studies on manganese, rhenium, iron, ruthenium and platinum as a central metal [7,8]. Now we have extended these studies to aryl complexes and their protonation reaction, with the aim of synthesising new σ-bonded κ^1-aryl complexes and testing whether η^2-coordination of an aromatic ring can take place. The results of these studies, which involve the synthesis and some reactivity of rare examples of aryl complexes of manganese and rhenium, are reported here.

2. Experimental

2.1. General considerations and physical measurements

All synthetic work was carried out under an appropriate atmosphere (Ar, H$_2$) using standard Schlenk techniques or

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a Vacuum Atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored under an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. The $Re_2(CO)_{10}$ was a Pressure Chem (USA) product, while $Mn_2(CO)_{10}$ an Aldrich one, both used as received. The triethylphosphite $P(OEt)_3$ (Aldrich) was purified by distillation under nitrogen, while the $PPh(OEt)_2$ and the PPh_2OEt were prepared by the method of Rabinowitz and Pellon [9]. Phenyllithium Li[Ph] (2.0 M solution in di-n-butyl ether) was an Aldrich product, while p-tolyl lithium Li[4-$CH_3C_6H_4$] was prepared following the reported method [10]. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Spectrum One or a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra (^{1}H, ^{31}P, ^{13}C) were obtained on a Bruker AC200 or an AVANCE 300 spectrometers at temperatures varying between −90 and +30 °C, unless otherwise noted. ^{1}H and ^{13}C spectra are referred to internal tetramethylsilane, while $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed using their standard programs. The SwaN-MR software package [11] has been used in treating the NMR data. The conductivity of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83 instrument.

2.2. Synthesis of complexes

The hydride $ReH(CO)_{5-n}P_n$, $ReH(CO)_3[Ph_2PO(CH_2)_3OPPh_2]$ and $MnH(CO)_{5-n}P_n$ [P = $P(OEt)_3$, $PPh(OEt)_2$ and PPh_2OEt; $n = 2, 3$] complexes were prepared following the methods previously reported [7,12].

2.2.1. $Re(\kappa^1\text{-}C_6H_5)(CO)_{5-n}P_n$ (1, 3, 5) [n = 1 (1), n = 2 (3), n = 3 (5); P = P(OEt)_3 (a), PPh(OEt)_2 (b), PPh_2OEt (c)]

An equimolar amount of triflic acid (0.33 mmol, 29 μL) was added to a frozen solution of the appropriate hydride $ReH(CO)_{5-n}P_n$ (0.33 mmol) in 10 mL of toluene cooled to −196 °C. The reaction mixture was brought to room temperature, stirred for 1 h, cooled again to −196 °C and then an excess of Li[Ph] (0.50 mmol, 0.25 mL of a 2.0 M solution in di-n-butyl ether) was added. The resulting solution was brought to room temperature, stirred for 3 h and then the solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL). By cooling the resulting solution to −25 °C, pale-yellow microcrystals of the product separated out which were filtered and dried under vacuum; yield between 45 and 65%. Anal. Calc. for $C_{24}H_{20}O_5PRe$ (1c): C, 47.60; H, 3.33. Found: C, 47.77; H, 3.41. Calc. for $C_{21}H_{35}O_9P_2Re$ (3a): C, 37.11; H, 5.19. Found: C, 36.95; H, 5.25%. Calc. for $C_{29}H_{35}O_7P_2Re$ (3b): C, 46.83; H, 4.74. Found: C, 46.67; H, 4.90%. Calc. for

$C_{37}H_{35}O_5P_2Re$ (3c): C, 55.01; H, 4.37. Found: C, 54.83; H, 4.31%. Calc. for $C_{38}H_{50}O_8P_3Re$ (5b): C, 49.94; H, 5.51. Found: C, 50.08; H, 5.62%.

2.2.2. $Re(\kappa^1\text{-}C_6H_5)(CO)_3[Ph_2PO(CH_2)_3OPPh_2]$ (3d)

An equimolar amount of CF_3SO_3H (0.16 mmol, 14 μL) was added to a solution of the $[ReH(CO)_3\{Ph_2PO\text{-}(CH_2)_3OPPh_2\}]$ (0.12 g, 0.16 mmol) in 10 mL of toluene cooled to −196 °C. The reaction mixture was brought to room temperature, stirred for 1 h and then cooled again to −196 °C. An excess of Li[Ph] (0.8 mmol, 0.4 mL of a 2.0 M solution in di-n-butyl ether) was added and the resulting solution brought to room temperature and stirred for 3 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL). A white solid slowly separated out which was filtered off, washed with ethanol and dried under vacuum. Crystallization by slow evaporation of a solution of the compound in CH_2Cl_2 and ethanol (2:10 ratio) gave suitable crystals for X-ray analysis; yield 55%. Anal. Calc. for $C_{36}H_{31}O_5P_2Re$: C, 54.61; H, 3.94. Found: C, 54.55; H, 4.01%.

2.2.3. $Re(\kappa^1\text{-}4\text{-}CH_3C_6H_4)(CO)_{5-n}P_n$ (2, 4) [n = 1 (2), n = 2 (4); P = P(OEt)_3 (a), PPh(OEt)_2 (b), PPh_2OEt (c)]

An equimolar amount of CF_3SO_3H (0.33 mmol, 29 μL) was added to a solution of the appropriate hydride $ReH(CO)_{5-n}P_n$ (0.33 mmol) in 10 mL of toluene cooled to −196 °C. The reaction mixture was allowed to reach room temperature, stirred for 1 h and cooled again to −196 °C. An excess of Li[4-$CH_3C_6H_4$] (1.0 mmol, 2 mL of a 0.5 M solution in toluene) was added and the reaction mixture, brought to room temperature, stirred for 5 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol (2 mL). By cooling the resulting solution to −25 °C, pale-yellow microcrystals of the product were obtained which were filtered and dried under vacuum; yield between 55 and 65%. Anal. Calc. for $C_{25}H_{22}O_5PRe$ (2c): C, 48.46; H, 3.58. Found: C, 48.59; H, 3.71%. Calc. for $C_{22}H_{37}O_9P_2Re$ (4a): C, 38.09; H, 5.38. Found: C, 38.19; H, 5.26%. Calc. for $C_{30}H_{37}O_7P_2Re$ (4b): C, 47.55; H, 4.92. Found: C, 47.48; H, 4.90%. Calc. for $C_{38}H_{37}O_5P_2Re$ (4c): C, 55.54; H, 4.54. Found: C, 55.65; H, 4.63%.

2.2.4. $Mn(\kappa^1\text{-}C_6H_5)(CO)_3[P(OEt)_3]_2$ (6a)

This complex was prepared exactly like the related rhenium complex 3a starting from $MnH(CO)_3[P(OEt)_3]_2$; yield $\geqslant$ 55%. Anal. Calc. for $C_{21}H_{35}MnO_9P_2$: C, 46.00; H, 6.43. Found: C, 45.86; H, 6.56%.

2.2.5. $[Re(CO)_3P_2]BF_4$ (7) [P = P(OEt)_3 (a), PPh(OEt)_2 (b), PPh_2OEt (c)]

A slight excess of $HBF_4 \cdot Et_2O$ (0.15 mmol, 22 μL of a 54% solution) was added to a solution of the appropriate $Re(\kappa^1\text{-}C_6H_5)(CO)_3P_2$ complex 3 (0.12 mmol) in 5 mL of CH_2Cl_2 cooled to −196 °C. The reaction mixture was

brought to room temperature, stirred for 1 h and then the solvent removed under reduced pressure. The oil obtained was triturated with ethanol (1 mL) to give, after cooling to $-10\ °C$, a white solid which was filtered and dried under vacuum; yield $\geqslant 55\%$. Anal. Calc. for $C_{15}H_{30}BF_4O_9P_2Re$ (**7a**): C, 26.14; H, 4.39. Found: C, 26.24; H, 4.28. Calc. for $C_{23}H_{30}BF_4O_7P_2Re$ (**7b**): C, 36.67; H, 4.01. Found: C, 36.54; H, 3.90%. Calc. for $C_{31}H_{30}BF_4O_5P_2Re$ (**7c**): C, 45.54; H, 3.70. Found: C, 45.58; H, 3.81%.

2.3. X-ray crystal structure determination of Re(κ^1-C_6H_5)(CO)$_3$[Ph$_2$PO(CH$_2$)$_3$OPPh$_2$] (3d)

The data collection was taken on a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation. Absorption correction was carried out using SADABS [13].

The structure was solved by Patterson methods and refined by a full-matrix least-squares based on F^2 [14]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography [15]. Details of crystal data and structural refinement are given in Table 1. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 615621.

2.4. Protonation reactions

The protonation of the aryl complexes M(κ^1-Ar)(CO)$_{5-n}$P$_n$ (**1–6**) was carried out in an NMR tube, recording the spectra between -80 and $+20\ °C$. A typical experiment involves the preparation, in a screw-cap 5-mm NMR tube, of a solution of the appropriate aryl complex (20–30 mg, 0.02–0.03 mmol) in 0.5 mL of CH$_2$Cl$_2$. The tube is sealed, cooled to $-80\ °C$ and then either an equimolar or an excess amount of HBF$_4 \cdot$ Et$_2$O is added. The tube is transferred into the probe of the instrument, pre-cooled to $-80\ °C$, and the spectra recorded.

3. Results and discussion

3.1. Preparation of κ^1-aryl derivatives

Aryl complexes of rhenium of the Re(κ^1-Ar)(CO)$_n$P$_{5-n}$ types were prepared by allowing hydride ReH(CO)$_n$P$_{5-n}$ species to react first with triflic acid (HOTf) and then with an excess of LiAr, as shown in Scheme 1.

Also the Re(κ^1-C_6H_5)(CO)$_3$[Ph$_2$PO(CH$_2$)$_3$OPPh$_2$] (**3d**) complex, containing the bidentate phosphite ligand, was

Table 1
Crystal data and structure refinement for Re(κ^1-C_6H_5)(CO)$_3$[Ph$_2$PO(CH$_2$)$_3$OPPh$_2$] (**3d**)

Identification code	Pat
Empirical formula	$C_{36}H_{31}O_5P_2Re$
Formula weight	791.75
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 10.6066(8)$ Å
	$b = 12.2720(10)$ Å
	$c = 13.8461(11)$ Å
	$\alpha = 85.464(2)°$
	$\beta = 72.3950(10)°$
	$\gamma = 69.6790(10)°$
Volume	1610.3(2) Å^3
Z	2
Density (calculated)	1.633 Mg/m^3
Absorption coefficient	3.914 mm^{-1}
$F(000)$	784
Crystal size	$1.1 \times 0.8 \times 0.7$ mm^3
Theta range for data collection	1.77–28.00°
Index ranges	$-11 \leqslant h \leqslant 13, -9 \leqslant k \leqslant 16,$
	$-16 \leqslant l \leqslant 18$
Reflections collected	9994
Independent reflections	7029 [$R_{int} = 0.0214$]
Completeness to theta = 28.00°	90.4 %
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	1.000 and 0.452
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7029/0/397
Goodness-of-fit on F_2	1.016
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0306, wR_2 = 0.0691$
R indices (all data)	$R_1 = 0.0355, wR_2 = 0.0706$
Largest differences in peak and hole	1.949 and -1.552 e Å^{-3}

Scheme 1. Ar = C$_6$H$_5$ (**1**, **3**, **5**) 4-CH$_3$C$_6$H$_4$ (**2**, **4**); P = P(OEt)$_3$ (**a**), PPh(OEt)$_2$ (**b**), PPh$_2$OEt (**c**).

ReH(CO)$_3$(P–P) + HOTf $\xrightarrow{-H_2}$ Re(κ^1-OTf)(CO)$_3$(P–P) $\longrightarrow$

$\xrightarrow{\text{LiC}_6\text{H}_5}$

$$\text{3d}$$
$$(V)$$

MnH(CO)$_3$P$_2$ + HOTf $\xrightarrow{-H_2}$ Mn(κ^1-OTf)(CO)$_3$P$_2$ $\longrightarrow$

$\xrightarrow{\text{LiC}_6\text{H}_5}$

$$\text{6a}$$
$$(III)$$
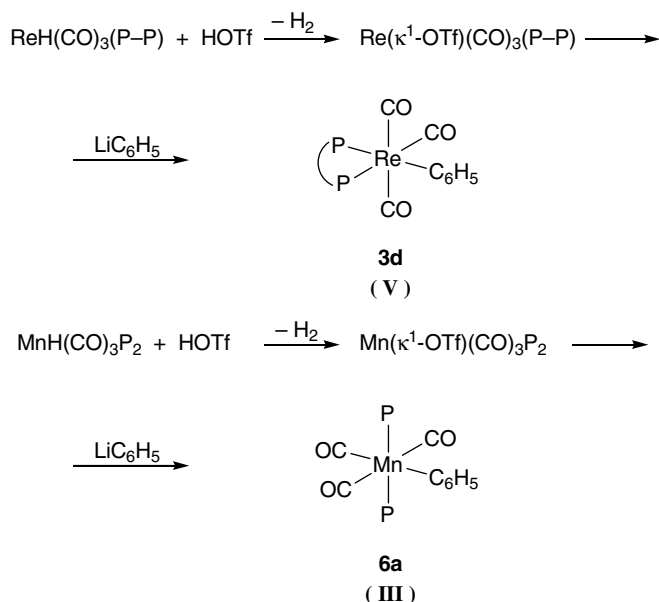
Scheme 2. P–P = Ph$_2$PO(CH$_2$)$_3$OPPh$_2$ (**d**); P = P(OEt)$_3$ (**a**).

prepared from the reaction of the triflate complexes with phenyllithium, as shown in Scheme 2. Furthermore, related aryl complexes of manganese Mn(κ^1-Ar)(CO)$_3$P$_2$ can be prepared using the hydride MnH(CO)$_3$P$_2$ as a precursor, but in this case only the tricarbonyl Mn(κ^1-C$_6$H$_5$)(CO)$_3$-[P(OEt)$_3$]$_2$ (**6a**) complex was separated as a solid (Scheme 2).

The reaction of both the manganese and rhenium hydride MH(CO)$_n$P$_{5-n}$ with triflic acid is known to proceed [7,12] with evolution of H$_2$ and formation of the triflate M(κ^1-OTf)(CO)$_n$P$_{5-n}$ complexes, which can undergo substitution of the labile κ^1-OTf ligand giving the final aryl derivatives **1–6**. Crucial for the synthesis of complexes **1–6** was the use of lithium aryls as reagents and to start the reaction at low temperature. Otherwise, only intractable mixtures of solid compounds were obtained. The use of Grignard's reagents MgBrAr, in fact, does not allow to prepare, in any conditions, κ^1-aryl derivatives of Mn and Re. Moreover, it may be noted that, in the case of manganese, only tricarbonyl Mn(κ^1-Ar)(CO)$_3$P$_2$ (**6**) complexes were obtained in pure form. With both related dicarbonyl Mn(κ^1-Ar)(CO)$_2$P$_3$ and tetracarbonyl Mn(κ^1-Ar)(CO)$_4$P precursors only decomposition products were obtained from the reaction with LiAr.

The aryl M(κ^1-Ar)(CO)$_n$P$_{5-n}$ (**1–6**) complexes were isolated as white (rhenium) or yellow (manganese) solids, stable in the air and in solution of the most common organic solvents, where they behave like non-electrolytes. Analytical and spectroscopic data (Tables 2 and 3) support the proposed formulations of the complexes, and a geometry in solution was also established. Furthermore, support for the formulation of the complexes comes from the X-ray crystal structure determination of Re(κ^1-C$_6$H$_5$)(CO)$_3$-[Ph$_2$PO(CH$_2$)$_3$OPPh$_2$] (**3d**) derivative, whose ORTEP is shown in Fig. 1. The rhenium atom in the complex is coor-

dinated by three *mer* carbonyl ligands, two phosphorus atoms of the bidentate phosphinite ligand Ph$_2$PO-(CH$_2$)$_3$OPPh$_2$, and a κ^1-*C*-coordinated benzene ring in a pseudooctahedral geometry, with *cis* angles ranging from 81.01(15) to 105.81(3)°, being the largest value that corresponding with the chelate angle. This P–Re–P angle, 105.81(3)°, is comparable to that found in similar rhenium(I) complexes [7c]. The steric requirements of the phenyl groups attached the phosphorus atoms seem to be the main source of distortion, as indicated by the angle value sequence   C(3)–Re–C(4) < C(3)–Re–P(1) < C(4)–Re–P(2) < P(2)–Re–P(1) (Table 4).

The Re–P bond lengths are 2.3924(10) and 2.4395(10) Å, the shorter corresponding to the phosphorus atom *trans* to the benzene ligand, which exerts less *trans* influence than the carbonyl ligand. The last value is similar to those reported for rhenium(I) complexes with this diphosphinite ligand [7c]. The three Re–C distances are in the expected range for tricarbonyl rhenium(I) complexes [7c], and they are in keeping with the expected *trans* influences: an average 1.965(4) Å for the mutually *trans* carbonyl ligands, slightly longer than 1.946(4) for the carbonyl *trans* to a phosphorus atom.

To our knowledge, there are not deposited any data in the Cambridge Crystallographic Data Centre [16] containing rhenium(I) metal center coordinated to a non substituted phenyl ring in a κ^1-*C*-fashion, although some complexes with κ-*C*-chelating ligands can be found [17]. The Re–C(Ph) distance, 2.222(4) Å is in the range found in the mentioned complexes, and it is a typical value for single σ-type C–Re bonds. The phenyl ring is coordinated is such a way that the rhenium atoms is only 0.170(7) Å from the plane defined by the ring (rms deviation of 0.0065 Å), and the Re–C4 bond made a 4.65° angle with the plane. The least-squares plane and the Re–C1 and Re–C2 bonds made angles of 23.73° and 18.33°, respectively, while the Re–C3 and Re–P2 bond (in *cis* respect to the phenyl ligand) made angles of 65.17° and 66.85° with the least-squares plane (see Newman type projection in Fig. 2).

The eight-membered chelate ring has a conformation similar to that found in other complexes of this ligand: [7c] the Re, P1, P2, O51 and O52 atoms are almost coplanar (rms deviation 0.0771 Å), C52 is only 0.178(6) Å from the plane they define and C53 and C51 are respectively 0.936(5) Å below and 0.730(5) Å above this plane (see Fig. 3).

The presence of the κ^1-aryl ligand in all **1–6** complexes is confirmed by both ^{1}H and ^{13}C NMR spectra which also allow, by means of COSY, HMQC and HMBC experiments, to assign the resonances of all the atoms of the aryl ligand (Tables 2 and 3). In particular, in the ^{1}H NMR spectra a multiplet appears at 6.93–6.30 ppm which is attributed to the protons in *ortho* position of the κ^1-aryl ligands. The signals of the other protons generally overlap those of the phenyl ring of the phosphine between 7.84 and 7.40 ppm and were identified by COSY experiments. In the ^{13}C

Table 2
IR and NMR data for the rhenium complexes

	Compound	Ir[a] (cm^{-1})	Assgnt	^{1}H NMR[b,c] δ (J, Hz)	Assgnt	Spin system	^{31}P{^{1}H} NMR[b,d] δ (J, Hz)
1c	Re(κ^1-C$_6$H$_5$)(CO)$_4$[PPh$_2$(OEt)]	1947 s, br 1925 m 1900 s	ν_{CO}	6.77 m 3.18 m 0.83 t	κ^1-C$_6$H$_5$ CH$_2$ CH$_3$	A	102.7 s
2c	Re[κ^1-(4-CH$_3$C$_6$H$_4$)](CO)$_4$[PPh$_2$(OEt)]	1955 s 1940 s 1916 s 1884 s	ν_{CO}	7.70 m 6.62 m 3.17 m 2.14 s 0.81 t	κ^1-C$_6$H$_4$ CH$_2$ CH$_3$ p-tolyl CH$_3$	A	102.2 s
3a	Re(κ^1-C$_6$H$_5$)(CO)$_3$[P(OEt)$_3$]$_2$	1969 s 1938 s 1904 s	ν_{CO}	7.84 m 6.85 m 3.78 m 1.17 t	κ^1-C$_6$H$_5$ CH$_2$ CH$_3$	A$_2$ A$_2$[e]	117.2 s 120.4 s
3b	Re(κ^1-C$_6$H$_5$)(CO)$_3$[PPh(OEt)$_2$]$_2$	1974 s 1938 s 1910 s	ν_{CO}	6.93 m 6.30 m 4.12 m 4.02 m 1.40 t	κ^1-C$_6$H$_5$ CH$_2$ CH$_3$	A$_2$	137.0 s
3c	Re(κ^1-C$_6$H$_5$)(CO)$_3$[PPh$_2$(OEt)]$_2$	2018 w 1953 s 1902 s	ν_{CO}	6.77 m[e] 3.16 m 0.81 t	κ^1-C$_6$H$_5$ CH$_2$ CH$_3$	A$_2$ [e]	102.7 s
3d	Re(κ^1-C$_6$H$_5$)(CO)$_3$[Ph$_2$PO(CH$_2$)$_3$OPPh$_2$]	2037 m 1956 s 1918 s	ν_{CO}	7.40 m 6.81 m 6.74 m 4.00–3.85 m 2.05 m	κ^1-C$_6$H$_5$ OCH$_2$ CH$_2$	AB[f]	δ_A 116.7 δ_B 114.9 J_{AB} = 23.0
4a	Re[κ^1-(4-CH$_3$C$_6$H$_4$)](CO)$_3$[P(OEt)$_3$]$_2$	2046 w 1942 s 1911 s	ν_{CO}	7.68 m 6.69 m 3.76 m 2.16 s 1.16 t	κ^1-C$_6$H$_4$ CH$_2$ CH$_3$ p-tolyl CH$_3$	A$_2$	116.9 s
4b	Re[κ^1-(4-CH$_3$C$_6$H$_4$)](CO)$_3$[PPh(OEt)$_2$]$_2$	1975 s 1946 s 1904 s	ν_{CO}	7.74 m 6.63 d 3.68 m 3.62 m 2.18 s 1.13 t	κ^1-C$_6$H$_4$ CH$_2$ CH$_3$ p-tolyl CH$_3$	A$_2$	133.2 s
4c	Re[κ^1-(4-CH$_3$C$_6$H$_4$)](CO)$_3$[PPh$_2$(OEt)]$_2$	2037 w 1956 s 1917 s	ν_{CO}	7.65 m 6.63 m 3.15 m 2.16 s 0.83 t	κ^1-C$_6$H$_4$ CH$_2$ CH$_3$ p-tolyl CH$_3$	A$_2$	102.3 s
5b	Re(κ^1-C$_6$H$_5$)(CO)$_2$[PPh(OEt)$_2$]$_3$	1973 s 1861 s	ν_{CO}	7.79 m 6.66 m 3.60 m 3.42 m 1.17 t 1.08 t	κ^1-C$_6$H$_5$ CH$_2$ CH$_3$	AB$_2$	δ_A 137.6 δ_B 136.9 J_{AB} = 37.9
6a	Mn(κ^1-C$_6$H$_5$)(CO)$_3$[P(OEt)$_3$]$_2$	2042 w 1954 s 1903 s	ν_{CO}	7.71 m 6.84 m 3.76 m 1.14 t	κ^1-C$_6$H$_5$ CH$_2$ CH$_3$	A$_2$	175.0 s, br
7a	[Re(CO)$_3${P(OEt)$_3$}$_2$]BF$_4$	1976 s 1953 s 1919 s	ν_{CO}	4.14 m 1.38 t	CH$_2$ CH$_3$	A$_2$	115.7 s
7b	[Re(CO)$_3${PPh(OEt)$_2$}$_2$]BF$_4$	1982 s 1952 s 1924 s	ν_{CO}	4.04 m 1.40 t	CH$_2$ CH$_3$	A$_2$	135.8 s

Table 2 (*continued*)

	Compound	Ir[a] (cm^{-1})	Assgnt	^{1}H NMR[b,c] δ (*J*, Hz)	Assgnt	Spin system	^{31}P{^{1}H} NMR[b,d]δ (*J*, Hz)
7c	[Re(CO)$_3${PPh$_2$(OEt)}]BF$_4$	1979 s	ν_{CO}	3.70 m	CH$_2$	A$_2$	110.7 s
		1956 s		1.24 t	CH$_3$		
		1921 s					

[a] In KBr pellets.
[b] In CD$_2$Cl$_2$ at 25 °C.
[c] Phenyl proton resonances of phosphite ligands between 7.70 and 7.20 ppm are omitted.
[d] Positive shifts downfield from 85% H$_3$PO$_4$.
[e] At −70 °C.
[f] In CDCl$_3$.

spectra, the resonances of the κ^1-bonded carbon atom (C *ipso*) appear as a triplet or a multiplet due to the coupling with the phosphorus nuclei of the phosphites and fall between 146 and 142 ppm (Table 3). The other carbon signals were identified between 146.5 and 142.1 ppm and confirm the presence of the κ^1-aryl ligands. The IR spectra of the tetracarbonyl M(κ^1-Ar)(CO)$_4$P (**1**, **2**) complexes in the CO stretching region show two broad absorptions for **1c** and four well-resolved bands for **2c**, in agreement with a mutually *cis* arrangement of the phosphite and the aryl ligand. Support for such a geometry (type **I**) comes from the ^{13}C NMR spectra of **1c**, which show three doublets between 189.3 and 188.6 ppm due to the carbonyl carbon resonances of inequivalent CO ligands, as expected for a *cis* geometry.

The IR spectra of the tricarbonyl complexes depends on the nature of the phosphite and of the aryl ligands. Three strong bands were observed in the ν_{CO} region of complexes **3a**, **3b**, **4b** suggesting a *fac* arrangement of the three carbonyl ligands, in agreement with type **II** geometry. As expected, in the temperature range between +20 and −80 °C, the ^{31}P NMR spectra show a sharp singlet, in agreement with the proposed geometry. The IR spectra of complexes **3c**, **4a**, **4c**, instead, show one medium-intensity ν_{CO} band and two strong ones, indicating a *mer* arrangement of the three carbonyl ligands. In the temperature range between +20 and −80 °C the ^{31}P NMR spectra appear as a sharp singlet, in agreement with the magnetic equivalence of the two phosphite ligands. On the basis of these data a *mer-trans* geometry **III** can reasonably be proposed for these tricarbonyl derivatives.

A *mer-cis* geometry **V**, like those found in the solid state, can be proposed for the Re(κ^1-C$_6$H$_5$)(CO)$_3$(P–P) (**3d**) compound. The IR spectra, in fact, show three ν_{CO} bands (one of medium intensity and two strong), while the ^{31}P NMR spectra display an AB quartet indicating the magnetic inequivalence of the two phosphorus atoms of the phosphine, as in type **V** geometry. A *mer-trans* geometry of type **III**, instead, may be proposed for the manganese Mn(κ^1-C$_6$H$_5$)(CO)$_3${P(OEt)$_3$}$_2$ (**6a**) complex, whose IR spectra show a weak band at 2042 cm^{-1} and two strong ones at 1954 and 1903 cm^{-1}. The ^{31}P spectra appear as a slightly broad singlet at room temperature, but already at −20 °C it results as a sharp singlet which remains unchanged until −90 °C, in agreement with the magnetic equivalence of the two phosphite ligands. On the basis of IR and NMR data,

a type **III** geometry can be reasonably proposed for the manganese derivative **6a**.

The IR spectrum of the dicarbonyl Re(κ^1-C$_6$H$_5$)(CO)$_2${PPh(OEt)$_2$}$_3$ (**5b**) complex shows two strong ν_{CO} bands at 1973 and 1861 cm^{-1} suggesting the mutually *cis* position of the two carbonyl ligands. These two CO ligands, however, are not magnetically equivalent because two well-separated multiplets for the carbonyl carbon resonances are present at 197.2 and at 196.8 ppm in the ^{13}C NMR spectrum. In the temperature range between +20 and −80 °C the ^{31}P{^{1}H} NMR spectrum appears as a AB$_2$ multiplet, in agreement with the presence of two magnetically equivalent phosphite ligands and different from the third. On the basis of these data, a *mer-cis* geometry **IV** can be proposed for our dicarbonyl derivative **5b**.

In contrast with the alkyl [18] [Re]–CH$_3$ and [Re]–C$_2$H$_5$ derivatives, aryl [Re]–Ar complexes of rhenium are rare and, apart from the pentacarbonyl Re(κ^1-Ar)(CO)$_5$ compounds [19], no other example of a stable compound have still been reported. The use of the mixed-ligand Re(κ^1-OTf)(CO)$_n$P$_{5-n}$ triflate complexes with phosphite and carbonyls as precursors allows the synthesis of new examples of this class of complexes.

3.2. Protonation reactions

The κ^1-aryl Re(κ^1-Ar)(CO)$_n$P$_{5-n}$ (**1**–**5**) complexes quickly react with HBF$_4$ · Et$_2$O in CH$_2$Cl$_2$ to give free hydrocarbon and the unsaturated [Re(CO)$_n$P$_{5-n}$]$^+$ cations which, in the case of tricarbonyls, were isolated as BF$_4$ salts and characterized (Scheme 3).

Free hydrocarbon is formed also from protonation of the related manganese complex **6a** but, in this case, no stable compound was isolated.
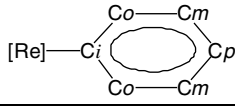
The reaction was studied at variable temperature by NMR spectra with the aim of testing whether protonation of the κ^1-aryl ligand can give an intermediate complex containing an arene molecule η^2-coordinate to the metal center.

Examples of metal complexes containing a phenyl ring coordinated in η^2-fashion are well known [3,4] and the protonation of the κ^1-aryl ligand in **1**–**6** should lead to the formation of an arene molecule in the coordination sphere of the metal allowing its η^2-coordination to the metal centers, as shown in Scheme 4.

Table 3
$^{13}C\{^1H\}$ NMR data for selected rhenium complexes

	Compound	$^{13}C\{^1H\}$ NMR[a,b] δ (J, Hz)	
1c	Re(κ^1-C$_6$H$_5$)(CO)$_4$[PPh$_2$(OEt)]	189.3 d	CO
		$J_{CP} = 45$	
		188.9 d	
		$J_{CP} = 10.5$	
		188.6 d	
		$J_{CP} = 7.5$	
		146.5 d	C ipso
		$J_{CP} = 11.3$	
		135.6 s	C ortho
		128.9 s	C meta
		121.4 s	C para
		64.0 d	CH$_2$
		16.3 d	CH$_3$
3b	Re(κ^1-C$_6$H$_5$)(CO)$_3$[PPh(OEt)$_2$]$_2$	191.0 t	CO
		$J_{CP} = 11.3$	
		189.2 t	
		$J_{CP} = 6.8$	
		142.1 t	C ipso
		128.8 s	C ortho
		128.3 s	C meta
		120.4 s	C para
		64.2 t	CH$_2$
		16.1	CH$_3$
3d	Re(κ^1-C$_6$H$_5$)(CO)$_3$[Ph$_2$PO(CH$_2$)$_3$OPPh$_2$]	197.0 dd	CO
		$J_{CP} = 2$	
		$J_{CP} = 49$	
		196.3 dd	
		$J_{CP} = 8$	
		$J_{CP} = 12$	
		147.3 s	C ortho
		142.5 dd	C ipso
		$J_{CP} = 10$	
		$J_{CP} = 18$	
		127.6 s	C meta
		122.2 s, br	C para
		61.3 s	OCH$_2$
		60.7 s	
		32.6 t	CH$_2$
		$J_{CP} = 5$	
4b	Re[κ^1-(4-CH$_3$C$_6$H$_4$)](CO)$_3$[PPh(OEt)$_2$]$_2$	195.0 t	CO
		$J_{CP} = 11.7$	
		193.6 t	
		$J_{CP} = 7.5$	
		146.5 s	C ortho
		142.8 t	C ipso
		$J_{CP} = 12.8$	
		130.5 s	C meta
		127.8 s	C para
		62.4 t	CH$_2$
		21.0 s	CH$_3$ p-tolyl
		16.0 t	CH$_3$ phos
5b	Re(κ^1-C$_6$H$_5$)(CO)$_2$[PPh(OEt)$_2$]$_3$	197.2 td	CO
		$J_{CP} = 11$	
		$J_{CP} = 2$	
		196.8 m	
		143.2 s	C ortho
		142.3 m	C ipso
		125.1 s	C meta
		122.4 s	C para

Table 3 (*continued*)

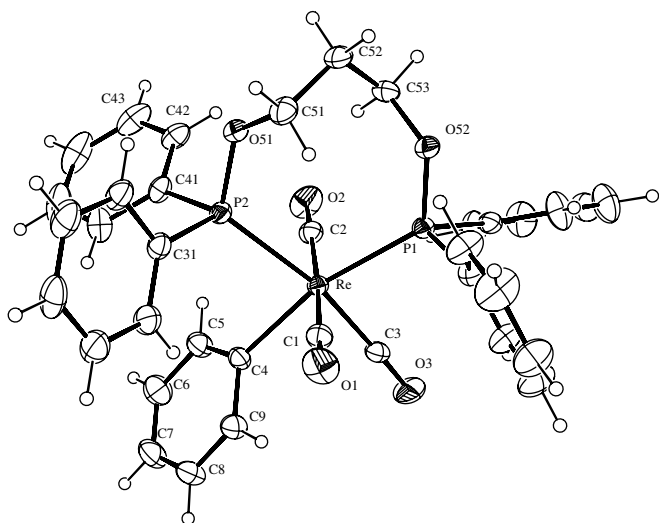| Compound	$^{13}C\{^1H\}$ NMR[a,b] δ (J, Hz)	
	62.3 m	CH_2
	16.3 t	CH_3
	16.1 t	
7c $[Re(CO)_3\{PPh_2(OEt)\}]BF_4$	191.7 t	CO
	$J_{CP} = 10$	
	190.9 t	
	$J_{CP} = 6$	
	64.5 t	CH_2
	15.6 t	CH_3

[a] In CD_2Cl_2 at 25 °C.
[b] Phenyl carbon resonances are omitted.

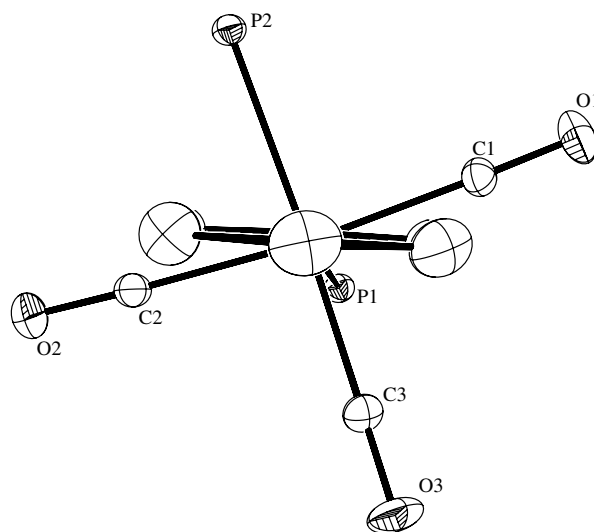Fig. 1. ORTEP view of the complex drawn with 30% thermal ellipsoids probability.

Fig. 2. View of the coordination sphere along the axis Ph–Re–P.

Table 4
Bond lengths (Å) and angles (°) for $Re(\kappa^1-C_6H_5)(CO)_3[Ph_2PO-(CH_2)_3OPPh_2]$ (**3d**)

Lengths			
Re–C(1)	1.974(4)	Re–C(2)	1.957(4)
Re–C(3)	1.946(4)	Re–C(4)	2.222(4)
Re–P(1)	2.3924(10)	Re–P(2)	2.4395(10)
Angles			
C(3)–Re–C(2)	92.79(17)	C(3)–Re–C(1)	92.82(18)
C(2)–Re–C(1)	174.38(16)	C(3)–Re–C(4)	81.01(15)
C(2)–Re–C(4)	91.66(16)	C(1)–Re–C(4)	89.45(16)
C(3)–Re–P(1)	86.25(12)	C(2)–Re–P(1)	93.48(12)
C(1)–Re–P(1)	86.65(13)	C(4)–Re–P(1)	166.48(10)
C(3)–Re–P(2)	167.86(12)	C(2)–Re–P(2)	85.22(12)
C(1)–Re–P(2)	89.35(13)	C(4)–Re–P(2)	87.07(10)
P(1)–Re–P(2)	105.81(3)		

Fig. 3. Detail of the chelate ring.

[**A**], according to the presence exclusively of the signals of free arene in the proton NMR spectra of the reaction mixture. From the protonation reaction, however, the formally unsaturated tricarbonyl $[Re(CO)_3P_2]BF_4$ (**7**) complexes can be isolated as white microcrystals and characterized.

Complexes **7** are stable as solids and in solution of polar organic solvents, where they behave like 1:1 electrolytes [20]. This result seems to exclude the coordination of the
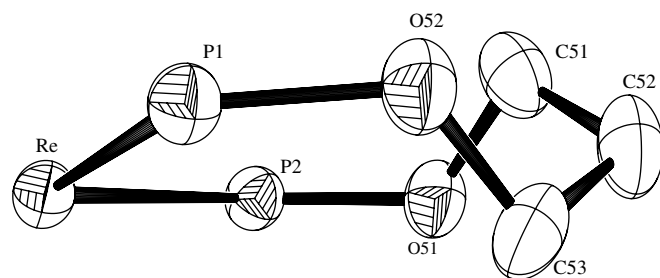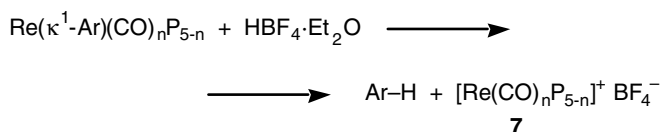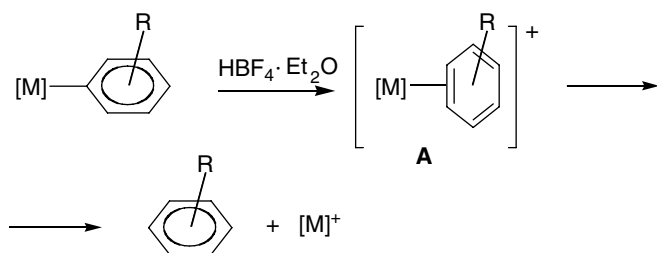
Unfortunately, even protonating the κ^1-aryl complexes at −80 °C, the ^1H NMR spectra do not give any evidence of the formation of the η^2-arene complex intermediate

$$Re(\kappa^1\text{-Ar})(CO)_nP_{5-n} + HBF_4\cdot Et_2O \longrightarrow$$

$$\longrightarrow Ar\text{–}H + [Re(CO)_nP_{5-n}]^+ BF_4^-$$
$$\textbf{7}$$

Scheme 3. $n = 3$ (**7**); P = P(OEt)$_3$ (**a**), PPh(OEt)$_2$ (**b**), PPh$_2$OEt (**c**).

Scheme 4. [M] = Re(CO)$_n$P$_{5-n}$ or Mn(CO)$_3$P$_2$.

BF$_4$ anion to give an octahedral Re(BF$_4$)(CO)$_3$P$_2$ complex. The hexacoordination of [Re(CO)$_3$P$_2$]$^+$ cation, however, can be reached either by coordination of one solvent molecule (CH$_2$Cl$_2$) [18c,21], or by agostic interaction [22] between the electron-deficient metal center and a CH bond of the ethyl (or phenyl) group of one phosphite ligand. Unfortunately, spectroscopic data do not give any conclusive information on the behaviour and the geometry in solution of these cations.

The IR spectra of the [Re(CO)$_3$P$_2$]BF$_4$ (**7**) complexes show in the ν_{CO} region three strong bands indicating a *fac* arrangement of the three carbonyl ligands. The NMR spectra, however, do not allow to unambiguously assign a geometry to the complexes, i.e. to distinguish between geometry **VI** and **VII** (Scheme 5).

In the temperature range between +20 and −80 °C, in fact, the profile of both the proton and the ^{31}P NMR spectra of complexes **7** do not change and even at −80 °C only one singlet is observed in the ^{31}P spectra indicating the magnetic equivalence of the two phosphite ligands. A geometry **VI** with one coordinate solvent molecule agrees with the observed spectra at this temperature, although also a geometry **VII**, in which the agostic C–H interaction is still fast interchanging from one of the phosphite ligands to the other, is in agreement with the presence of a singlet in the ^{31}P spectra. In the absence of an X-ray crystal struc-
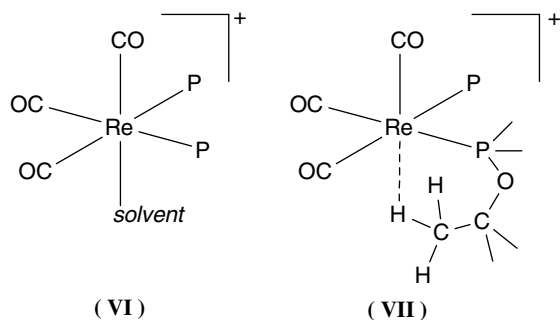
Scheme 5.

ture determination, therefore, no conclusion can be drawn on the geometry of these unsaturated complexes **7**.

4. Conclusions

In this paper we report the synthesis of a series of κ^1-aryl complexes of manganese and rhenium stabilized by carbonyl and phosphite ligands. The structural parameters for the Re(κ^1-C$_6$H$_5$)(CO)$_3$[Ph$_2$PO(CH$_2$)$_3$OPPh$_2$] derivative were also obtained. Studies on the protonation reactions of the aryl complexes with Brønsted acid highlighted the formation of free hydrocarbons and the unsaturated [M(CO)$_n$P$_{5-n}$]$^+$ cations.

Acknowledgement

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