member of the two CF_3 groups doublet at ϕ 75.4 is reduced to a single septet while the higher field member is unaltered. Likewise, when the higher field member of the PF_2 group doublet (at ϕ 58.1) is irradiated, the resonance at ϕ 76.4 is converted to a septet leaving the resonance of lower field member unchanged.

The ^{31}P spectra of several of the compounds were measured. The resonances are divided into triplets with further small couplings. That of $(CF_3)_2C(N_3)OP({=}O)F_2$ shows a resonance centered at 394 cps, that of $(CF_3)_2C(NCS)OP({=}O)F_2$ at 451 cps, that of $(CF_3)_2C(CN)OP({=}S)F_2$ at 414 cps, and that of $(CF_3)_2C(CN)OPF_2$ at -1505 cps. A compound, $(CF_3)_2C(I)OPF_2$, prepared previously[2] shows a resonance centered at -1728 cps. The trend in δ values is in the direction opposite to that expected from a change of oxidation state of the phosphorus atom. It is also observed that the ^{31}P resonance of the thiophosphate(V) ester is centered at lower field than those of the corresponding phosphate compounds.

The ultraviolet spectrum of $(CF_3)_2C(NCS)OP({=}O)F_2$ is typical for an isothiocyanato derivative. Both λ_{max} (249 mμ) and ϵ_{max} (621) are consistent with other published results.[17]

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(17) M. F. Lappert and H. Pyzora, *J. Chem. Soc.*, 854 (1967).

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Olefin–Phosphine Complexes of Manganese(I) and Rhenium(I)

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Monoolefin complexes of manganese(I) and rhenium(I) have been prepared using the bidentate olefin phosphine ligands 2-*cis*-propenylphenyldiphenylphosphine (*cis*-PP), 2-allylphenyldiphenylphosphine (AP) and 2-styrylphenyldiphenylphosphine (SP). These include neutral $LM(CO)_3X$ species (where L = *cis*-PP, AP, or SP and X = halide) and also complexes containing $LM(CO)_4{}^+$ cations. Coordination of both the olefin and the phosphorus atom in these complexes is evidenced by infrared and nmr spectral data. The results of the infrared spectral measurements are discussed in terms of the bonding between olefin and metal.

Introduction

It has been shown that air-stable monoolefin complexes of the zerovalent group VI transition metals[2–5] as well as derivatives of Pt(II),[6,7] Pd(II),[7] Ag(I), and Cu(I)[8] can be prepared through the use of bidentate olefin–phosphine ligands. We now report the extension of this series of chelated monoolefin complexes to include derivatives of the type $LM(CO)_3X$ (L = olefin–phosphine ligand; M = Mn, Re; X = halogen) and $[LM(CO)_4{}^+]Y^-$ (Y^- = monovalent anion).

Although a wide variety of carbonyl-containing univalent group VII metal complexes are known,[9] very few of these contain coordinated monoolefins.[10,11] Indeed, the olefin–phosphine derivatives of Re(I) described herein apparently have been precedented only by the $[(C_2H_4)_2Re(CO)_4][AlCl_4]$ complex reported by Fischer and Oefele.[11] In addition to the interest in these complexes as further members of a new class of chelated olefin derivatives, their preparation offers an opportunity to study, in a more direct fashion than was previously possible, the effect of the charge on the metal upon the metal–olefin bond strength. In the case of the metal carbonyls it appears that a decrease in the electron density on the metal lowers the metal–carbon bond order, presumably owing to inhibition of π bonding between the metal and the CO groups.[12,13] This decrease in electron density may be accomplished either by attaching groups of increasing electronega-

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(1) General Electric Research and Development Center, Schenectady, N. Y. 12301.

(2) M. A. Bennett, L. V. Interrante, and R. S. Nyholm, *Z. Naturforsch.*, **20b**, 633 (1965).

(3) L. V. Interrante, M. A. Bennett, and R. S. Nyholm, *Inorg. Chem.*, **5**, 2212 (1966).

(4) M. A. Bennett, R. S. Nyholm, and J. D. Saxby, *J. Organometal. Chem.* (Amsterdam), **7**, 301 (1967).

(5) The crystal structure of one of these complexes has recently been determined by three-dimensional X-ray diffraction measurements: H. Luth, M. R. Truter, and A. Robson, *Chem. Commun.*, 738 (1967).

(6) M. A. Bennett, H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 4570 (1964).

(7) M. A. Bennett, W. R. Kneen, and R. S. Nyholm, *Inorg. Chem.*, **7**, 556 (1968).

(8) M. A. Bennett, W. R. Kneen, and R. S. Nyholm, *ibid.*, **7**, 552 (1968).

(9) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959); A G. Osborne and M. H. B. Stiddard, *ibid.*, 4715 (1962); B. Chiswell and L. M. Venanzi, *ibid.*, *A*, 417 (1966).

(10) W. R. McClellan, U. S. Patent 2,990,418 (June 27, 1961); *Chem. Abstr.*, **56**, 1480*e* (1962); W. Strohmeier and H. Helman, *Chem. Ber.*, **98**, 1598 (1965); E. O. Fischer and K. Oefele, *Angew. Chem.*, **73**, 581 (1961); M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.* (Amsterdam), **1**, 58 (1963).

(11) E. O. Fischer and K. Oefele, *Angew. Chem. Intern. Ed. Engl.*, **1**, 52 (1962).

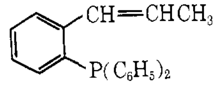
(12) M. A. Bennett and R. J. H. Clark, *J. Chem. Soc.*, 5560 (1964).

(13) R. W. Cattrall and R. J. H. Clark, *J. Organometal. Chem.* (Amsterdam), **6**, 167 (1966).

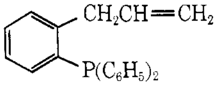
tivity to the same metal ion, as in the series $Mn(CO)_5I$, $Mn(CO)_5Br$, $Mn(CO)_5Cl$,[12] or, more directly, through the use of isoelectronic and isostructural species of increasing formal positive charge, *i.e.*, $V(CO)_6^-$, $Cr(CO)_6$, $Mn(CO)_6^+$.[13] For metal–olefin complexes only the first of these two methods has previously been available.[14,15] The $[LM(CO)_4^+]Y^-$ complexes, along with their isoelectronic group VI counterparts,[3] now provide a more direct means of varying the charge on the metal and thus assessing the importance of π-bonding in metal-olefin complexes.

Experimental Section

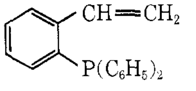
Starting Materials.—The unsaturated tertiary phosphines used in this study were 2-*cis*-propenylphenyldiphenylphosphine, $(C_6H_5)_2PC_6H_4CH{=}CHCH_3$ (*cis*-PP), 2-allylphenyldiphenylphosphine, $(C_6H_5)_2PC_6H_4CH_2CH{=}CH_2$ (AP), and 2-styryldiphenylphosphine, $(C_6H_5)_2PC_6H_4CH{=}CH_2$ (SP)



cis-PP



AP



SP

cis-PP was prepared as outlined below and AP by the method described earlier.[3] SP was a gift from Dr. W. Kneen of University College, London. The manganese pentacarbonyl halides were prepared by direct reaction between $Mn_2(CO)_{10}$ and the appropriate halogen[9,16] and were sublimed before use. Rhenium pentacarbonyl chloride was prepared by treating a carbon tetrachloride solution of $Re_2(CO)_{10}$ with a slow stream of dry chlorine gas for 30 min. The $Re(CO)_5Cl$ was rinsed with water and recrystallized from carbon tetrachloride before use.

Preparation of 2-*cis*-Propenylphenyldiphenylphosphine (*cis*-PP).—The preparation followed the procedure described previously[3] except for the initial synthesis of 2-*trans*-propenylchlorobenzene, which was carried out according to the method of Kharasch and Fuchs.[17] Anhydrous cobaltous chloride (15 g, 0.12 mol) was added to a Grignard reagent prepared from 317 g (1.65 mol) of *o*-chlorobromobenzene and 40.2 g (1.65 g-atom) of magnesium in 200 ml of ether. After stirring for 45 min a solution of 200 g (1.65 mol) of *trans*-1-bromo-1-propene in 150 ml of ether was added dropwise, while cooling in an ice bath, followed by 1 hr of reflux. After hydrolyzing with 10% HCl the ether layer was separated, dried, and distilled at atmospheric pressure. The residue was distilled under reduced pressure to give a 32% yield (80.3 g) of 2-*trans*-propenylchlorobenzene (bp 59–69° (4 mm)). The subsequent enrichment in *cis* isomer by uv irradiation, separation of isomers, and reaction with magnesium and chlorodiphenylphosphine in tetrahydrofuran was carried out as previously described.[3]

Preparation of Complexes. $LM(CO)_3X$ (L = *cis*-PP, AP, SP; M = Re, X = Cl; M = Mn, X = Cl, Br, I).—These complexes were prepared in benzene solution by displacement of CO from the $M(CO)_5X$ complexes under nitrogen. In a typical preparation 1–2 mmol of the $M(CO)_5X$ complex was stirred at 50° with an equimolar amount of the ligand in 50 ml of benzene for 3–4 hr. After removing the benzene under reduced pressure the residue was rinsed with cold pentane and then recrystallized from hexane to give air-stable crystals of the $LM(CO)_3X$ complex in 65–75% yield. The colors of the manganese complexes range from yellow in the case of the X = Cl derivatives to red for those containing I, whereas the $LRe(CO)_3Cl$ complexes are colorless. The compounds are soluble in benzene and chloroform, slightly soluble in hexane, and insoluble in water. One of these complexes was analyzed for carbon monoxide by measuring the amount of CO released upon oxidation of the complex with bromine. $(AP)Mn(CO)_3Br$ was treated with excess Br_2 in a closed, evacuated tube and the CO released was measured using a Toepler pump. After 48 hr at 50° an amount of CO equivalent to 2.8 mol/mol of complex was obtained.

$[LM(CO)_4][M'Cl_4]$. Method A. High-Pressure Synthesis of $[LRe(CO)_4][FeCl_4]$ (L = *cis*-PP, AP, SP).—The complexes of this type were prepared by the procedure of Kruck and Noack,[18] in which chloride is replaced by carbon monoxide under pressure using $FeCl_3$ as a Cl^- acceptor. A mixture of 0.30–1.50 g of $LRe(CO)_3Cl$ and excess $FeCl_3$ (2–3 mol/mol of complex) was added to a 40-ml rocking autoclave and charged to 5800 psi with carbon monoxide. After *ca.* 70 hr at 35° the contents of the bomb were removed to a sintered-glass funnel and rinsed with *ca.* 100 ml of ethyl ether. Concentration of the ether filtrate and cooling to 0° gave a *ca.* 5–10% yield of the $[LRe(CO)_4][FeCl_4]$ complexes. A low yield of the corresponding $[LMn(CO)_4][FeCl_4]$ derivatives could also be obtained by this procedure; however, these were more conveniently prepared as the $AlCl_4^-$ salts by method B. The $[LRe(CO)_4][FeCl_4]$ salts were obtained by this procedure as pale yellow crystals and were moderately soluble in polar organic solvents, such as acetonitrile, tetrahydrofuran, and ethanol, and soluble in water.

Method B. Atmospheric Pressure Preparation of $[LMn(CO)_4][AlCl_4]$ (L = *cis*-PP, AP, SP).—The procedure used to prepare these complexes was a modification of the method described by Kruck and Hoefler.[19] In this procedure carbon monoxide was bubbled through a benzene solution of the complex $LMn(CO)_3Cl$ (1.0 mmol) and anhydrous $AlCl_3$ (2.0–2.5 mmol) for 30 min with stirring. The solution assumed a pale yellow color, and an oily, red-orange layer separated. After discarding the supernatant solution, the oil was rinsed with ethyl ether which converted it to a light yellow solid. The ether was then removed by filtration and the solid was purified by reprecipitation from its filtered tetrahydrofuran solution with ether. A 60–90% yield of the $[LMn(CO)_4][AlCl_4]$ complexes was obtained by this method as highly moisture sensitive, pale yellow crystals. These complexes were soluble in acetone, acetonitrile, and tetrahydrofuran, were insoluble in chloroform, ether, and benzene, and were decomposed by water and methanol to give $LMn(CO)_3Cl$. Attempts to prepare the $[LRe(CO)_4][AlCl_4]$ complexes by this method gave only a very small yield of the expected product admixed with large amounts of starting material.

Attempted Direct Reaction of SP with $Mn(CO)_6^+$ Salts. Reaction with $[Mn(CO)_6][FeCl_4]$.—Equimolar amounts of $[Mn(CO)_6][FeCl_4]$[18] and SP were refluxed for 30 hr in 40 ml of tetrahydrofuran. Only decomposition products of the ligand and the original $[Mn(CO)_6][FeCl_4]$ were recovered. There was no evidence of substitution.

Reaction of SP with $[Mn(CO)_6][ClO_4]$.—Equimolar amounts of $[Mn(CO)_6][ClO_4]$[19] and SP were stirred and refluxed in THF for 9.5 hr. Substitution and decomposition of the ligand were evidenced by the infrared spectrum; however, the desired product was not obtained. The substitution product appeared to be $(SP)Mn(CO)_3Cl$ by infrared comparison.[20]

Anion-Exchange Reactions. Preparation of $[(AP)Re(CO)_4][B(C_6H_5)_4]$.—An impure sample of $[(AP)Re(CO)_4][AlCl_4]$ (*ca.* 0.5 g), prepared in an incomplete reaction according to method B, was extracted with ether giving a colorless solution which was filtered and then partitioned with water. A solution of $NaB(C_6H_5)_4$ in water was then added to the aqueous layer to give a white precipitate which was rinsed with ether and dried, *in vacuo;* yield of $[(AP)Re(CO)_4][B(C_6H_5)_4]$, *ca.* 6% based upon $(AP)Re(CO)_3Cl$. This salt was soluble in acetone, slightly soluble in water and ethanol, but insoluble in ether.

Preparation of $[LRe(CO)_4][PF_6]$.—After extraction of the

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[14] P. D. Kaplan and M. Orchin, *Inorg. Chem.*, **4**, 1393 (1965).

[15] R. G. Denning and L. M. Venanzi, *J. Chem. Soc., A*, 336 (1967); S. I. Shupack and M. Orchin, *J. Am. Chem. Soc.*, **85**, 902 (1963).

[16] R. B. King, "Organometallic Synthesis," Vol. 1, Academic Press Inc., New York, N. Y., 1965, pp 174–175, and references therein.

[17] M. S. Kharasch and C. F. Fuchs, *J. Am. Chem. Soc.*, **65**, 504 (1943).

[18] T. Kruck and M. Noack, *Chem. Ber.*, **96**, 3028 (1963).

[19] T. Kruck and M. Hoefler, *ibid.*, **96**, 3035 (1963).

[20] The chloride presumably came from reduction of perchlorate; *cf.* E. W. Abel and S. P. Tyfield, *Chem. Commun.*, 465 (1968).

$[LRe(CO)_4][FeCl_4]$ reaction product with ether (see preparation of $[LRe(CO)_4][FeCl_4]$, method A) the remaining solid was further extracted with *ca.* 100 ml of water. The resulting solution was filtered and then treated with a saturated aqueous solution of NH_4PF_6 which produced a white precipitate. This product was collected by filtration and recrystallized from ethanol to give an additional 8–15% yield of the $LRe(CO)_4^+$ complexes as the respective PF_6^- salts. These salts were obtained as long, colorless needles, soluble in acetone and ethanol, slightly soluble in water, and insoluble in ether. Both of these derivatives and the previously described $[(AP)Re(CO)_4][B(C_6H_5)_4]$ complex were quite resistant to oxidation and would be handled in air as the solid or in solution without noticeable decomposition. The molar conductivities of two of these salts, $[(cis\text{-PP})Re(CO)_4][PF_6]$ and $[(SP)Re(CO)_4][PF_6]$, were measured in acetone solution at *ca.* 10^{-3} *M* concentration. The values obtained, 154 and 160, respectively, are very close to those previously observed for other cationic rhenium carbonyl complexes under similar conditions of solvent and concentration.[18,19]

Measurements.—Infrared spectra were obtained in CCl_4 and $CDCl_3$ solutions as well as in the solid state as Nujol mulls, using a Perkin-Elmer Model 421IR spectrophotometer. The infrared spectra in the C=C stretching region were separately measured using the instrument on expanded-scale operation and were carefully calibrated with polystyrene film. In addition, several of the spectra were independently determined on a Perkin-Elmer 521IR spectrophotometer on expanded-scale operation with H_2O vapor as calibrant.[21] In each of these cases the observed position of the band assigned to the C=C stretching frequency was within 2–3 cm^{-1} of that measured using the Model 421 instrument. Nujol mulls of the $AlCl_4^-$ and $FeCl_4^-$ derivatives were all prepared under nitrogen in a drybox. The nmr spectrum of the $(cis\text{-PP})Mn(CO)_3Br$ complex was recorded on a Varian HR 100 spectrometer in $CDCl_3$ solution using *ca.* 1% tetramethylsilane (TMS) as an internal standard. Attempts to obtain nmr spectra of the $[LM(CO)_4][Y]$ complexes were frustrated by the limited solubility of these salts in solvents suitable for the determination. Microanalyses and molecular weight measurements were performed by the microanalytical laboratory of the University of California and are reported in Table I.

Results

The olefin–phosphine derivatives of the group VII metal pentacarbonyl halides were prepared by direct reaction in benzene solution at 50°. As evidenced by elemental analyses, molecular weight data (Table I), and measurement of the CO released upon oxidation of one of the complexes with Br_2, in each case 2 mol of CO is replaced by 1 mol of ligand to give monomeric compounds of the general formula $LM(CO)_3X$ (L = *cis*-PP, AP, SP; M = Mn, X = Cl, Br, I; M = Re, X = Cl). These complexes all exhibit three strong bands in the CO stretching region of the infrared spectra (Table II) as expected for *cis*-disubstituted $Mn(CO)_5X$ derivatives.[22]

Additional evidence for coordination of the olefin portion of these ligands to the metal is provided by the infrared spectra shown in Figure 1. The 1642-cm^{-1} (6.09-μ) band assigned to the C=C stretching frequency of the free *cis*-PP ligand is clearly absent from the spectrum of the $(cis\text{-PP})Mn(CO)_3Cl$ complex; however, unlike the group VI complexes of this ligand the coordinated C=C stretching frequency does not fall in the

TABLE I

ANALYTICAL AND MOLECULAR WEIGHT DATA

Compound		% C Calcd.	% C Found	% H Calcd.	% H Found	% Halogen Calcd.	% Halogen Found	% P Calcd.	% P Found	Mol. Wt. Calcd.[a]	Mol. Wt. Found[b]
$LMn(CO)_3X$											
L	X										
cis-PP	Cl	60.50	60.70	4.03	4.22	7.44	7.18	6.50	6.37	477	476
cis-PP	Br	55.40	55.42	3.68	3.63	15.34	15.56	5.94	6.02	521	515
cis-PP	I	50.80	51.00	3.38	3.59	22.35	22.42	5.45	5.36	568	524
AP	Cl	60.50	60.90	4.03	4.07	7.44	7.18	6.50	6.38	477	451
AP	Br	55.40	55.28	3.68	3.68	15.34	15.46	5.94	5.85	521	487
AP	I	50.80	51.09	3.38	3.67	22.35	22.06	5.45	5.26	568	555
SP	Cl	59.90	59.60	3.68	3.88	7.69	7.89	6.71	6.44	462	464
SP	Br	54.30	54.72	3.38	3.64	15.75	15.62	6.11	6.11	507	504
SP	I	49.90	49.69	3.10	3.44	22.90	22.66	5.59	5.60	554	535
$LRe(CO)_3Cl$											
L											
cis-PP		47.43	47.78	3.15	3.17	5.84	5.78	5.10	4.88	...	...
AP		47.43	47.23	3.15	3.30	5.84	5.98	5.10	5.06	608	607
SP		46.53	46.71	2.87	3.09	5.20	5.11	5.95	5.68	---	---
$[LMn(CO)_4]AlCl_4$											
L											
cis-PP		47.10	46.86	2.98	3.17	22.28	22.18	4.86	4.75	---	---
AP		47.10	47.36	2.98	3.39	22.28	22.29	4.86	4.42	---	---
SP		46.20	46.23	2.73	3.10	22.80	21.98	4.97	5.20	---	---
$[LRe(CO)_4]A$											
L	A										
cis-PP	$FeCl_4$	37.62	37.85	2.40	2.52	17.77	17.99	3.89	3.49	---	---
cis-PP	PF_6	40.29	40.11	2.56	2.51	---	---	8.30	8.25	---	---
AP	$FeCl_4$	37.62	37.39	2.40	2.19	17.77	17.81	3.89	3.82	---	---
AP	PF_6	40.29	39.62	2.56	2.70	---	---	8.30	7.93	---	---
AP	$B(C_6H_5)_4$	64.00	63.85	4.28	4.53	---	---	3.37	3.20	---	---
SP	$FeCl_4$	36.81	36.56	2.19	2.10	18.08	18.31	3.94	3.89	---	---
SP	PF_6	39.47	39.68	2.34	2.48	---	---	8.46	8.23	366	365

[a] Assuming molecular weight = formula weight of complex except for $[LRe(CO)_4]A$ in which case the Calcd. value = formula weight/2. [b] All the values for the $LM(CO)_3X$ complexes were obtained in chloroform solution at *ca.* 10^{-3} *M* concentration by vapor pressure lowering. The molecular weight of $[(SP)Re(CO)_4]PF_6$ was measured in acetone solution at the same concentration.

TABLE II

C–O STRETCHING FREQUENCIES FOR THE $LM(CO)_3X$ COMPLEXES

L	M	X	Freq, cm^{-1} [a,b]		
cis-PP	Mn	Cl	2045	1985	1923
cis-PP	Mn	Br	2044	1984	1920
cis-PP	Mn	I	2039	1980	1926
AP	Mn	Cl	2051	1989	1926
AP	Mn	Br	2047	1988	1926
AP	Mn	I	2044	1987	1930
SP	Mn	Cl	2051	1987	1929
SP	Mn	Br	2048	1985	1928
SP	Mn	I	2038	1975	1928
cis-PP	Re	Cl	2047	1985	1905
AP	Re	Cl	2054	1984	1905
SP	Re	Cl	2053	1981	1912

[a] All absorption bands strong. [b] Determined in carbon tetrachloride solution.

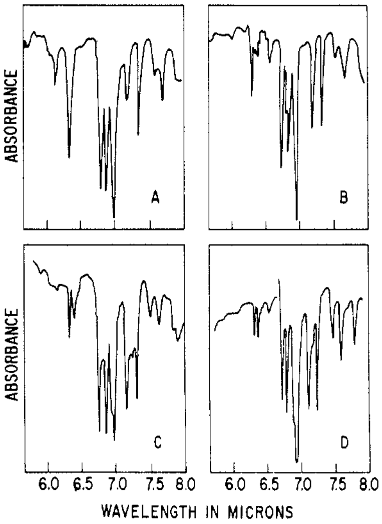

Figure 1.—Infrared spectra of 2-*cis*-propenylphenyldiphenylphosphine (*cis*-PP) and its complexes: A, *cis*-PP in deuteriochloroform; B, $(cis\text{-PP})Cr(CO)_4$ in deuteriochloroform; C, $(cis\text{-PP})Mn(CO)_3Cl$ in deuteriochloroform; D, $[(cis\text{-PP})Mn(CO)_4]AlCl_4$ in Nujol (*ca.* 5.5–6.7 μ) and in hexachlorobutadiene (6.7–8.0 μ) mulls.

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[21] We are grateful to R. Chrenko and D. McClung of the General Electric Research and Development Center Analytical Chemistry Operation for these measurements.

[22] R. J. Angelici, F. Basolo, and A. J. Poe, *J. Am. Chem. Soc.*, **85**, 2215 (1963).

TABLE III: INFRARED DATA FOR THE OLEFIN–PHOSPHINE LIGANDS AND REPRESENTATIVE GROUP VI, VII, AND VIII METAL COMPLEXES (1700–650 CM^{-1})[a,b]

	L = *cis*-PP						L = AP						L = SP					
Assignment	L[c]	LCr-(CO)$_4$[c]	LMn-(CO)$_3$Cl	LRe-(CO)$_3$Cl	[LMn-(CO)$_4$]-[AlCl$_4$]	[LRe-(CO)$_4$][PF$_6$]	L[c]	LPtBr$_2$[c]	LMn-(CO)$_3$Cl	LRe-(CO)$_3$Cl	[LMn-(CO)$_4$]-[AlCl$_4$]	[LRe-(CO)$_4$]-[PF$_6$]	L	LCr-(CO)$_4$[d]	LMn-(CO)$_3$Cl	LRe-(CO)$_3$Cl	[LMn-(CO)$_4$]-[AlCl$_4$]	[LRe-(CO)$_4$]-[PF$_6$]
C=C str	1644 vw	1525 vw, b	?	?	1541 vw	1525 vw	1637 w	1492 sh	?	?	1532 vw	1520 vw	1627 w	1505 w, b	?	?	1519 vw	1515 vw
	1582 w	1582 w	1592 vw	1585 vw	1585 vw	1596 vw	1587 w	1587 w	1598 w	1598 w	1587 w	1591 w	1580 vw		1582 vw	1582 vw	1588 vw	1580 vw
		1567 vw, b	1576 vw	1569 vw	1569 vw	1571 vw	1563 vw	1570 vw	1574 vw	1574 vw	1565 vw	1567 vw			1565 vw	1567 vw		
Arom ring str	1479 w	1484 w	1488 w	1488 w	1484 w	1480 w	1478 w	1482 w	1488 w	1486 w	1480 w	1477 w	1480 w	1480 w	1478 m	1479 m	1472 m	1480 m
	1460 w	1462 w	1468 w	1468 w	1465 w	1466 w	1464 w	1471 w	1439 m	1438 m			1460 w	1470 m	1468 m	1469 m		
Aliph C—H def	1435 m	1435 m	1440 m	1440 m	1435 m	1429 m	1435 m	1435 m	1420 w	1421 w	1439 m	1435 m	1435 m	1435 s	1439 m	1440 m	1433 m	1435 m
	1397 vw	1391 w	1403 w	1403 w	1399 w	1398 w	1406 sh	1383 vw	1398 vw	1399 vw	1399 vw	1395 vw	1405 vw	1390 w	1389 w	1390 w	1395 w	1399 w
	1364 w	1364 w	1376 w	1376 w	1365 w	1362 w												
Arom and olef C—H in-plane def	1325 vw	1326 vw	1338 vw	1338 vw	1327 vw	1327 vw	1323 sh	1326 vw	1331 vw	1332 vw	1333 vw	1329 vw	1325 vw	1256 w	1327 vw	1328 vw	1333 vw	1333 vw
	1307 vw	1305 vw	1317 vw	1316 vw	1307 vw	1297 vw	1307 vw	1305 vw	1313 vw	1315 vw	1310 vw	1309 vw	1307 w	1245 w	1304 vw	1307 vw	1310 vw	1310 vw
	1091 w, b	1095 m	1098 m	1098 m	1097 m	1083 m	1087 w	1092 m	1098 m	1098 m	1091 m	1092 m	1090 vw	1094 m	1090 m	1090 m	1099 m	1097 m
			1048 vw	1048 vw	1051 vw	1051 vw							989 vw	998 m	995 mw	995 mw	991 mw	996 mw
	1025 mw	1034 mw	1034 vw	1032 vw	1024 vw	1025 vw	1027 w	1020 mw	1033 vw	1034 vw	1031 mw	1022 vw	924 w	937 w				
	927 w	907 w, b	917 w	917 w	910 w	918 w	908 m				906 m				849 w	847 w		
	814 mw	817 w	825 w	825 w	825 w	824 w		765 m	767 w	767 w	765 m	766 w	786 vw	793 w	787 w	787 w	800 w	792 w
Arom and olef C—H out-of-plane def			805 w	805 w	806 w	806 w			755 s	755 s	753 s	759 s	769 mw	773 m	764 m	764 m	770 m	761 m
	767 ms	761 m	760 m	760 m	765 m	764 m	748 s	750 s	748 s	747 s	751 s	750 s	750 m	747 m	748 s	750 s	751 s	754 s
	743 ms	748 ms	752 ms	750 ms	742 ms	743 ms		711 w	710 w	709 w	704 w	717 w	742 s	740 m			741 m	741 m
		704 ms	707 ms	707 ms	707 ms	702 ms	696 s	700 vs	697 vw	697 vw	697 vw	696 vw		703 s	701 s	702 s	705 s	703 s
	694 s	693 ms	693 ms	693 ms	694 ms	689 ms		688 s	674 m	674 m	674 s	676 m	694 s	690 w	690 w	691 w	695 w	697 w
		664 s	664 s	664 s	685 s	684 s			665 s	665 s				671 s	664 s	664 s	680 s	678 s
P—F str						851 s, b						845 s, b						843 s, b

[a] For the LM(CO)$_3$X complexes: 1700–1200 cm^{-1}, CDCl$_3$ solution; 1200–650 cm^{-1}, Nujol mull. All other spectra determined as Nujol mulls. [b] s, strong; m, medium; w, weak; v, very; b, broad; ?, uncertain. [c,d] Data from ref 3 and 4, respectively, except for C=C streching frequencies which were independently determined from Nujol mull spectra.

1480–1580-cm^{-1} window provided by the ligand, and owing to the strong ligand absorption bands outside of this region an unambiguous assignment of this vibration could not be made. Similar spectra were obtained for the remaining LM(CO)$_3$X complexes (Table III) and in no case was it possible to assign the coordinated C=C stretching vibration with any reasonable degree of certainty.

It is apparent from the infrared data in Table III that the complexes prepared from AP and *cis*-PP are not identical and therefore that the isomerization of AP to *cis*-PP observed in the case of the group VI complexes[3] does not occur under the conditions used in the preparation of the group VII derivatives. In fact, comparison of the spectral data for the LM(CO)$_3$X complexes with that obtained for the free ligands, and their Pt(II) and their group VI metal complexes (Table III), shows that each of the olefin–phosphine ligands retains its structural identity upon coordination to the group VII metals.

In the case of the *cis*-PP and AP complexes this was also evidenced by displacement of the coordinated ligand in refluxing pyridine and its subsequent identification by infrared spectroscopy. Moreover, the nmr spectrum obtained for the (*cis*-PP)Mn(CO)$_3$Br complex clearly shows the 1:1:3 pattern characteristic of the coordinated –CH=CHCH$_3$ group.[3] However, the chemical shift values observed in this case (−6.02, −5.20, and −2.10 ppm relative to TMS) were about 0.1–0.6 ppm farther downfield than those obtained for the group VI metal complexes,[3] possibly reflecting the higher effective positive charge on the metal in the case of the manganese complex.[14]

Upon reaction of the LM(CO)$_3$Cl (L = *cis*-PP, AP, SP; M = Mn, Re) complexes with carbon monoxide in the presence of AlCl$_3$ or FeCl$_3$, the coordinated Cl$^-$ is replaced by CO to give cationic tetracarbonyl complexes of the type [LM(CO)$_4^+$][M'Cl$_4^-$] (M' = Al, Fe). In addition to elemental analyses and conductivity and molecular weight measurements (Table I), the formation of these LM(CO)$_4^+$ cations is evidenced, in the case of the Re derivatives, by the preparation of complexes in which B(C$_6$H$_5$)$_4^-$ and PF$_6^-$ replace M'Cl$_4^-$ as the associated anion (Table I). Furthermore, the position, number, and relative intensities of the infrared bands obtained for these complexes in the CO stretching region (Table IV) are entirely consistent with that expected for *cis*-octahedral LM(CO)$_4^+$ cations.[3,4,23] As with the LM(CO)$_3$X complexes, coordination of the carbon–carbon double bond is evidenced by the absence of the bands attributed to the uncoordinated C=C stretching frequency. However, in direct contrast to the LM(CO)$_3$X case, a new band does appear in the 1480–1580-cm^{-1} region of these spectra enabling assignment of the coordinated C=C stretching frequency (Figure 1, Table III).

The close correspondence between these spectra and the spectra of the appropriate group VI and Pt(II) complexes (Table III) indicates that no appreciable

[23] L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

TABLE IV

C–O STRETCHING FREQUENCIES FOR THE $[LM(CO)_4][M'Cl_4]$ COMPLEXES

L	M	M′	Freq, cm^{-1} [a]			
cis-PP	Mn	Al	2114 ms	2046 ms	2034 s	2000 vs
cis-PP	Re	Fe	2120 ms	2053 ms	2034 s	1993 vs
AP	Mn	Al	2112 ms	2053 ms		2025 vs
AP	Re	Fe	2130 ms	2060 ms	2036 s	2007 vs
SP	Mn	Al	2107 ms	2051 s		2016 vs
SP	Re	Fe	2131 ms	2060 ms	2030 s	2002 vs

[a] Determined as Nujol mulls.

change in the structure of the ligands occurs upon addition of CO to the $LM(CO)_3X$ complexes and, furthermore, that the $(cis\text{-}PP)M(CO)_4^+$ cations must be structurally analogous to their isoelectronic group VI counterparts.

Discussion

According to the Dewar[24]–Chatt[25] theory of the bonding in metal–olefin complexes, to a large extent the metal–olefin bond owes its existence to the capacity of the olefin to accept electron density from the metal as well as to donate it. This capacity presumably resides in the π^*-antibonding molecular orbital of the olefin which can overlap with filled d orbitals on the metal. The observation that olefins form only very weak complexes with metals incapable of such π interaction attests to its importance in metal–olefin bonding.[25,26] Moreover, it has been shown that changes in the nature of either the olefin or the metal which tend to favor the "back-donation" of electron density from the metal to the olefin increase the metal–olefin bond strength. Thus, the substitution of electron-withdrawing groups such as $-(CH_2)_nLR_3$ ($n = 1, 2$; L = N, As, P; R = H, CH_3),[27] –F,[28] and –CN[29] for one or more of the hydrogen atoms on ethylene appears to result in more stable metal–olefin complexes with many transition metals. Furthermore, substituents on the metal which tend to increase its π-electron density have also been found to produce stronger metal–olefin bonding.[14,15]

One way of assessing the degree of interaction between the olefin and metal is through measurement of the change in the C=C stretching frequency upon coordination of the olefin. According to the Dewar–Chatt theory, both the σ (L→M) and π (M→L) interactions between the olefin and the metal decrease the C=C bond order and thus lower the C=C stretching frequency. Indeed, the magnitude of this lowering in C=C stretching frequency ($\Delta\nu$(C=C)) appears to correlate well with the stability of metal–olefin complexes and has been widely used as a measure of the metal–olefin bond strength[25,30,31] in spite of the fact that the C=C stretching vibration is not always entirely independent of the other vibrational modes of the complex.[32]

The $\Delta\nu$(C=C) data for the group VII complexes of the type $[LM(CO)_4{}^+]Y^-$ are presented in Table V along with the values previously obtained for the corresponding isoelectronic group VI metal complexes. The significantly lower values obtained for the Mn(I) and Re(I) complexes are quite consistent with earlier conclusions[14,15] regarding the influence of the charge on the metal upon the metal–olefin interaction and provide strong support for the supposition that π bonding not only occurs in but is in fact the dominant feature of metal–olefin bonding.

TABLE V

SHIFT IN C=C STRETCHING FREQUENCY UPON COMPLEXATION ($\Delta\nu$(C=C))[a]

Compound	L		
	cis-PP	AP	SP
$[LMn(CO)_4][AlCl_4]$	103	105	108
$[LCr(CO)_4]$	119	. . .	120
$[LRe(CO)_4][PF_6]$	119	117	112
$[LW(CO)_4]$	139	. . .	135

[a] Derived from Nujol mull data using C=C stretching frequencies reported in Table III plus additional data from ref 4 as well as an independent measurement on the $(cis\text{-}PP)W(CO)_4$ complex [C=C stretching frequency = 1505 cm^{-1}].

The observation that the $\Delta\nu$(C=C) values are, to a first approximation, independent of the particular ligand chosen provides support for both the assignments of the individual C=C stretching frequencies and the supposition that $\Delta\nu$(C=C) is applicable as a measure of the metal–olefin bond strength in these complexes.

It should also be noted that the change in $\Delta\nu$(C=C) within the group VII series, *i.e.*, Re(I) > Mn(I), follows the same pattern as was previously observed for group VI[3] and group VIII[31] metal–olefin complexes in that the heaviest member of the group appears to interact most strongly with the C=C bond.

Although the data in Table V reveal no consistent trend in $\Delta\nu$(C=C) with variation of the olefin, the experimental uncertainty in these $\Delta\nu$(C=C) values (estimated at *ca.* 6–8 cm^{-1}) could easily conceal small changes in metal–olefin bond strength among the complexes of the three ligands. On the other hand, a distinct difference in the π-bonding capacity of these ligands does appear to be evidenced by the C—O stretching frequency data in Tables II and IV. In particular the complexes of AP and SP are observed to give consistently higher C—O frequencies than those of *cis*-PP suggesting that the C=C bond in the latter cases is not competing as successfully for the π-electron density on the metal.[33] This decrease in the π-acceptor

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(24) M. J. S. Dewar, *Bull. Soc. Chim. France*, **18**, C79 (1951).

(25) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(26) G. Hata, *Chem. Commun.*, 7 (1968).

(27) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc., A*, 324 (1967).

(28) R. Cramer, *J. Am. Chem. Soc.*, **89**, 4621 (1967).

(29) W. H. Baddley, *ibid.*, **90**, 3705 (1968).

(30) F. R. Hartley and L. M. Venanzi, *J. Chem. Soc., A*, 333 (1967).

(31) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **13**, 69 (1958).

(32) In particular, a strong coupling between the C=C stretching vibration and the $C{<}^{H}_{H}$ scissoring mode has recently been evidenced in the case of $K[(C_2H_4)PtCl_3]\cdot H_2O$: M. J. Grogan and K. Nakamoto, *J. Am. Chem. Soc.*, **88**, 5454 (1966).

(33) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959); F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).