(1937.6 cm^{-1}) < Ph$_2$ (1940.3 cm^{-1}). This agrees with predictions of the increased π-acceptor ability[34,35] of tertiary phosphines containing a larger number of phenyl groups in place of alkyl groups[2,15,35] and does not seem consistent with steric factors in this series of ligands although steric factors might be expected to be more prominent in a four-membered ring.

In summary, the syntheses of a new series of five ligands of the type $Ph_2PCH_2PR^1R^2$ (where $R^1 = R^2$ = Me or *i*-Pr and R^1 = Ph, R^2 = Me, Et, or *i*-Pr) and of 12 group 6 metal carbonyl derivatives of the type $[Ph_2PCH_2PR^1R^2]M(CO)_4$ (where $R^1 = R^2$ = Me or *i*-Pr; R^1 = Ph, R^2 = Me or *i*-Pr, and M = Cr, Mo, or W) are reported. These compounds are an important component in a larger study of unsymmetrical bis-phosphorus chelating ligands and their coordination compounds which contain various-sized chelate rings. Extensive ^{31}P and ^{1}H NMR results are reported.

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Registry No. $L_ICr(CO)_4$, 62264-03-3; $L_IMo(CO)_4$, 62264-04-4; $L_IW(CO)_4$, 62264-05-5; $L_{II}Cr(CO)_4$, 62264-06-6; $L_{II}Mo(CO)_4$, 62264-07-7; $L_{II}W(CO)_4$, 62264-08-8; $L_{III}Cr(CO)_4$, 62264-09-9; $L_{III}Mo(CO)_4$, 62264-10-2; $L_{III}W(CO)_4$, 62264-11-3; $L_{IV}Cr(CO)_4$, 62264-12-4; $L_{IV}Mo(CO)_4$, 62264-13-5; $L_{IV}W(CO)_4$, 62264-14-6; L_I, 62263-64-3; L_{II}, 62263-65-4; L_{III}, 62263-66-5; L_{IV}, 62263-67-6; Ph_2PCH_2PPhEt, 62263-68-7; $Ph_2P(S)CH_2PPh$(*i*-Pr), 54006-27-8; $Ph_2P(S)CH_2PPhEt$, 54006-30-3; $Ph_2P(S)CH_2PPhMe$, 54006-29-0; $Ph_2P(S)CH_2P$(*i*-Pr)$_2$, 54006-31-4; $Ph_2P(S)CH_2PMe_2$, 23176-51-4; Ph_2PMe, 1486-28-8; Ph_2PCH_2Li, 62263-69-8; Ph(*i*-Pr)PCl, 54006-34-7; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $C_7H_8Mo(CO)_4$, 12146-37-1.

Supplementary Material Available: Figures 1, 2, 4, and 6 showing NMR spectra (4 pages). Ordering information is given on any current masthead page.

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Unsymmetrical Bis-Phosphorus Ligands. 11. Group 6 Metal Carbonyl Derivatives of 1-(Diphenylphosphino)-3-(alkylphenylphosphino)propane[1,2]

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Nine new compounds of the type $[Ph_2P(CH_2)_3PPhR]M(CO)_4$, where R = Me, Et, or *i*-Pr and M = Cr, Mo, or W, have been synthesized and characterized by proton and phosphorus nuclear magnetic resonance and infrared spectroscopy. The disulfide derivatives, $Ph_2P(S)(CH_2)_3P(S)PhR$, of the ligands are also reported. It is demonstrated that J_{PP} in these six-membered chelate rings and in the corresponding analogues containing five- and four-membered chelate rings, $[Ph_2P(CH_2)_2PR^1R^2]M(CO)_4$ and $[Ph_2PCH_2PR^1R^2]M(CO)_4$, is a sum of two identifiable components: a contribution via the ligand backbone and a contribution via the metal center, such that $J_{PP} = J^B{}_{PP} + J^M{}_{PP}$.

Previous studies of group 6 metal carbonyl complexes with unsymmetrical di(tertiary phosphine) ligands, $Ph_2P(CH_2)_nPR^1R^2$, with $n = 1$[2] or 2,[3,4] have been reported. These ligands form four- and five-membered chelate rings, respectively. This paper reports similar complexes with $Ph_2P(CH_2)_3PPhR$,[5] with R = Me, Et, or *i*-Pr, which form six-membered chelate rings, and compares the phosphorus-31 NMR results for each series and the variation of chemical shifts and coupling constants with ring size.

Experimental Section

The physical measurements were carried out as described in the preceding paper.[2] The ligands were synthesized as previously reported.[5] Disulfides of the ligands were prepared by the reaction of a slight

Table I. Analytical Data for $Ph_2P(CH_2)_3PPhR$ Derivatives

	% C		% H		% P	
Compd	Calcd	Found	Calcd	Found	Calcd	Found
$[Ph_2P(CH_2)_3PPhEt]Cr(CO)_4$	61.36	60.90	4.96	5.12	11.72	11.95
$[Ph_2P(CH_2)_3PPhEt]Mo(CO)_4$	56.65	56.89	4.58	4.84	10.82	10.54
$[Ph_2P(CH_2)_3PPhEt]W(CO)_4$	49.11	48.56	3.97	3.85	9.28	9.01
$[Ph_2P(CH_2)_3PPh(i\text{-}Pr)]Cr(CO)_4$	61.99	62.07	5.20	5.34	11.42	11.07
$[Ph_2P(CH_2)_3PPh(i\text{-}Pr)]Mo(CO)_4$	57.35	57.97	4.81	4.88	10.56	10.04
$[Ph_2P(CH_2)_3PPh(i\text{-}Pr)]W(CO)_4$	49.87	49.88	4.19	4.33	9.19	9.44
$Ph_2P(S)(CH_2)_3P(S)PhMe$	63.75	63.48	5.84	5.96	14.95	14.60
$Ph_2P(S)(CH_2)_3P(S)PhEt$	64.46	63.79	6.12	6.42	14.46	13.85

Table II. Phosphorus-31 NMR Data for $Ph_2P(CH_2)_3PPhR$ and Derivatives

Species	δ_{PPh_2},[a] ppm	δ_{PPhR},[a] ppm	Δ_{PPh_2},[b] ppm	Δ_{PPhR},[b] ppm	J_{PP}, Hz	J_{WP}, Hz
$Ph_2P(CH_2)_3PPhMe$ (L_I)	−17.6	−34.2			0	
L_IS_2	41.7	38.7	59.3	72.9	0	
$L_ICr(CO)_4$	40.7	22.7	58.3	56.9	40.8	
$L_IMo(CO)_4$	20.1	1.0	37.7	35.2	28.5	
$L_IW(CO)_4$	−0.4	−21.4	17.2	12.8	22.6	222 (PPh_2) 216 (PPhMe)
$Ph_2P(CH_2)_3PPhEt$ (L_{II})	−17.4	−21.8			0	
$L_{II}S_2$	41.7	48.4	59.1	70.2	0	
$L_{II}Cr(CO)_4$	41.3	32.7	58.7	54.5	40.6	
$L_{II}W(CO)_4$	−0.1	−7.5	17.3	14.3	22.0	222 (PPh_2) 218 (PPhEt)
$Ph_2P(CH_2)_3PPh(i\text{-}Pr)$ (L_{III})	−18.0	−9.5			0	
$L_{III}S_2$	41.5	56.7	59.5	66.2	0	
$L_{III}Cr(CO)_4$	41.8	41.8	59.8	51.3		
$L_{III}Mo(CO)_4$	20.4	26.5	38.4	36.0	29.9	
$L_{III}W(CO)_4$	−0.3	7.0	17.7	16.5	22.7	221 (PPh_2) 220 (PPh(*i*-Pr))
$Ph_2P(CH_2)_3PPh_2$ (L)	−17.3					
$LCr(CO)_4$[c]	41.4		58.7			
$LMo(CO)_4$[c]	21.0		38.3			
$LW(CO)_4$[c]	0		17.3			222

[a] Positive values are downfield from 85% H_3PO_4. Samples were dissolved in CH_2Cl_2. [b] $\Delta = \delta_{complex} - \delta_{free\ ligand}$. [c] Reference 6.

excess of S with the ligand in hot benzene. Prepared in this manner were $Ph_2P(S)(CH_2)_3P(S)PhMe$, mp 72–74 °C, $Ph_2P(S)(CH_2)_3P(S)PhEt$, mp 160–162 °C, and $Ph_2P(S)(CH_2)_3P(S)Ph(i\text{-}Pr)$, mp 52–56 °C. Microanalyses are given in Table I and phosphorus-31 NMR data are given in Table II. Proton NMR results for the methyl region are given below.

The metal carbonyl complexes were prepared on a 0.01-mol scale by the direct reaction of the ligand and $Cr(CO)_6$, $Mo(CO)_6$, or $W(CO)_6$ in 1:1 molar ratio in 50 mL of hot diglyme under N_2 for about 1–2 h. The temperatures were 120–130 °C for the Cr and Mo compounds and 160–170 °C for the W compounds. The methyl compounds were oily due to slight impurities and did not give satisfactory analyses, but the ^{31}P NMR assignments were unequivocal for the expected compounds. Analytical data for the remaining compounds are given in Table I, and ^{31}P data, in Table II.

Proton NMR results for the methyl groups follow. Chemical shifts are in ppm downfield from TMS and coupling constants are in Hz. Doublet and triplet are represented by d and t, respectively. $[Ph_2P(CH_2)_3PPhMe]M(CO)_4$: Cr, 1.74 (d), $^2J_{PCH} = 7.5$; Mo, 1.75 (d), $^2J_{PCH} = 5.5$; W, 1.85 (d), $^2J_{PCH} = 7.0$. $[Ph_2P(CH_2)_3PPhEt]M(CO)_4$: Cr, 0.90, $^3J_{PCCH} = 15.0$, $^3J_{HCCH} = 8.5$; Mo, 0.77 (d of t), $^3J_{PCCH} = 15.5$, $^3J_{HCCH} = 7.5$; W, 0.90 (d of t), $^3J_{PCCH} = 14.5$, $^3J_{HCCH} = 6.5$. $[Ph_2P(CH_2)_3PPh(i\text{-}Pr)]M(CO)_4$: Cr, Me_a, 1.24 (d of d), $^3J_{PCCH} = 16.0$, $^3J_{HCCH} = 7.0$; Cr, Me_b, 1.00 (d of d), $^3J_{PCCH} = 13.5$, $^3J_{HCCH} = 7.0$; Mo, Me_a, 1.16 (d of d), $^3J_{PCCH} = 16.0$, $^3J_{HCCH} = 8.0$; Mo, Me_b, 1.15 (d of d), $^3J_{PCCH} = 18.0$, $^3J_{HCCH} = 8.0$; W, Me_a, 1.10 (d of d), $^3J_{PCCH} = 15.0$, $^3J_{HCCH} = 7.0$; W, Me_b, 1.08 (d of d), $^3J_{PCCH} = 17.5$, $^3J_{HCCH} = 7.0$.

Results and Discussion

Nine compounds of the type $[Ph_2P(CH_2)_3PPhR]M(CO)_4$, where R = Me, Et, or *i*-Pr and M = Cr, Mo, or W, have been prepared by reaction of the unsymmetrical di(tertiary phosphines) with the group 6 metal carbonyls. This series of compounds with six-membered chelate rings complements the previously reported analogues with four- and five-membered chelate rings. Relatively few ^{31}P NMR studies have been reported on chelating phosphorus ligands forming six-membered rings, although several recent ones have appeared,[6-8] which describe mainly platinum[7] and rhodium[8] compounds.

Since these new ligands have chemically and magnetically different phosphorus atoms, the phosphorus-31 NMR spectra have the expected pair of doublets arising from a simple AX group, except for $[Ph_2P(CH_2)_3PPh(i\text{-}Pr)]Cr(CO)_4$, in which the accidental coincidence of the resonances of the two phosphorus atoms results in a sharp singlet with no observable coupling. Although numerous phosphorus–phosphorus coupling constants for *cis*-$L_2M(CO)_4$ compounds, where L is a phosphorus donor and M is Cr, Mo, or W, have been tabulated previously,[9] only a relatively small number have been measured for the two donor atoms being tertiary phosphines. Other ligands include phosphites,[10] halophosphines,[11] PH_3,[12] and phosphorus–nitrogen[13] compounds. Since these different types of phosphorus ligands have different spin coupling properties,[9] relatively few examples of tertiary phosphine couplings are available for comparison. It is observed, however, that the magnitude of $|J_{PP}|$ for the compounds reported here increases in the same order (W < Mo < Cr) found for *cis*-$L_2M(CO)_4$ compounds.[10b]

The coordination shifts for the diphenylphosphino group in these ligands which form six-membered chelate rings are consistent with the previous observations for 1,3-bis(diphenylphosphino)propane,[6] viz., about 58, 38, and 17 ppm for the Cr, Mo, and W compounds, respectively. The coordination shifts for the alkylphenylphosphino groups are slightly smaller,

Table III. Average J_{PP} (Hz) for $[Ph_2P(CH_2)_nPR^1R^2]M(CO)_4$

M	$n = 1$	$n = 2$	$n = 3$
None	114	28	0
Cr	24	12	41
Mo	15	5	28
W	21	4	22

Table IV. Average Observed and Calculated Values of J_{PP} (Hz)[a] for $[Ph_2P(CH_2)_2PR^1R^2]M(CO)_4$

M	${}^3J^B{}_{PP}$[b]	${}^2J^M{}_{PP}$[c]	J_{PP} (possible values)[d]	J_{PP} (found)
Cr	30	41	71 or 11	12
Mo	30	28	58 or 2	5
W	30	22	52 or 8	4

[a] All coupling constants are absolute values. Signs were not determined. [b] Component of the coupling constant transmitted through the backbone; value assumed to be the same as J_{PP} in $(OC)_5MPPh_2(CH_2)_2PR^1R^2M(CO)_5$. [c] Component of the coupling constant transmitted through the metal center; value assumed to be the same as for $[Ph_2P(CH_2)_3PR^1R^2]M(CO)_4$. [d] $|J_{PP}| = |J^B{}_{PP} \pm J^M{}_{PP}|$.

Table V. Average Observed and Calculated Values of J_{PP} (Hz)[a] for $[Ph_2PCH_2PR^1R^2]M(CO)_4$

M	${}^2J^B{}_{PP}$[b]	${}^2J^M{}_{PP}$[c]	J_{PP} (possible values)[d]	J_{PP} (found)
Cr	12	41	53 or 29	23
Mo	12	28	40 or 16	15
W	12	22	34 or 10	21

[a] All coupling constants are absolute values. Signs were not determined. [b] Ligand backbone component of the coupling constant; see text. [c] Metal center component of the coupling constant; see text. [d] $|J_{PP}| = |J^B{}_{PP} \pm J^M{}_{PP}|$.

Table VI. Infrared Data[a] in the Carbonyl Stretching Region for $[Ph_2P(CH_2)_3PPhR]M(CO)_4$

Compd	Freq, cm^{-1}
$[Ph_2P(CH_2)_3PPhMe]Cr(CO)_4$	2008, 1940, 1899, 1890
$[Ph_2P(CH_2)_3PPhMe]Mo(CO)_4$	2020, 1950, 1932, 1904
$[Ph_2P(CH_2)_3PPhMe]W(CO)_4$	2020, 1942, 1927, 1895
$[Ph_2P(CH_2)_3PPhEt]Cr(CO)_4$	2010, 1926, 1899, 1890
$[Ph_2P(CH_2)_3PPhEt]Mo(CO)_4$	2020, 1929, 1905, 1900
$[Ph_2P(CH_2)_3PPhEt]W(CO)_4$	2020, 1924, 1899, 1894
$[Ph_2P(CH_2)_3PPh(i\text{-}Pr)]Cr(CO)_4$	2015, 1922, 1897, 1891
$[Ph_2P(CH_2)_3PPh(i\text{-}Pr)]Mo(CO)_4$	2020, 1929, 1905, 1900
$[Ph_2P(CH_2)_3PPh(i\text{-}Pr)]W(CO)_4$	2020, 1922, 1898, 1895

[a] Measured in C_6H_{12} solution.

by a few ppm, than that of the diphenylphosphino group in the same compound. This is opposite the trend generally observed for the four- and five-membered ring analogues and probably reflects the more important steric requirements of the large diphenylphosphino group (compared to methylphenylphosphino and ethylphenylphosphino) in the smaller rings. Other factors being equal, a stronger coordinate bond is probably reflected in a larger coordination shift.

The most interesting facet of these investigations arises from a comparison of the phosphorus–phosphorus coupling constants in these series of compounds. The thesis that we originally proposed is that coupling is transmitted via the two paths in the chelate ring,[6] i.e., through the ligand backbone ($J^B{}_{PP}$) and through the metal center ($J^M{}_{PP}$), and that the observed coupling is a sum of these two, such that

$$J_{PP} = J^B{}_{PP} + J^M{}_{PP}$$

From the data collected in these studies, we shall attempt to show that this is a plausible hypothesis, if the Karplus-type angular dependence of the coupling constants[14] in the flexible ring systems is minimal. In the 1,3-bis(phosphino)propanes and their disulfides ${}^4J^B{}_{PP}$ is nil. We assume that ${}^4J^B{}_{PP}$ will also be zero in the chelate, thus $J_{PP} = {}^2J^M{}_{PP}$; or since the signs have not been determined,[15] $|J_{PP}| = |{}^2J^M{}_{PP}|$. Table III gives the average J_{PP}'s observed for the compounds $[Ph_2P(CH_2)_nPR^1R^2]M(CO)_4$, where $n = 1$, 2, or 3 and M = Cr, Mo, or W. The nine average numbers in Table III are obtained from the data for 29 metal complexes of this type. Thus, we conclude that $|{}^2J^{Cr}{}_{PP}| = 41$ Hz, $|{}^2J^{Mo}{}_{PP}| = 28$ Hz, and $|{}^2J^{W}{}_{PP}| = 22$ Hz.

For the case where $n = 2$, i.e., the five-membered chelate ring, an independent measure of ${}^3J^B{}_{PP}$ can be obtained from the model compounds $(OC)_5MPh_2P(CH_2)_2PR^1R^2M(CO)_5$, in which the ligand bridges two metal centers and in which no coupling through the metal center is possible. The value of $|{}^3J^B{}_{PP}|$ is about 30 Hz.[3] Thus, by using this value for $J^B{}_{PP}$ and by assuming ${}^2J^M{}_{PP}$ remains the same in the six- and five-membered rings,[16] the results given in Table IV are obtained. As one can see, the results are quite good: $|J_{PP}|$ for Cr observed 12 Hz, calculated 11 Hz; for Mo observed 5 Hz, calculated 2 Hz; for W observed 4 Hz, calculated 8 Hz.

For the case where $n = 1$, the assumptions used are more precarious but the overall hypothesis seems reasonably valid. The model compound analogous to the $n = 2$ case, viz., $(OC)_5MPPh_2CH_2PR^1R^2M(CO)_5$, was not successfully synthesized although several attempts were made.[17] However, ${}^2J_{PCP}$ for compounds in which both phosphorus atoms are quadruply connected lie in a fairly narrow range; e.g., $|{}^2J_{PCP}|$ for $[Ph_2P(S)CH_2PMe_3]Br$ is 12 Hz.[18] We assume that $|{}^2J^B{}_{PP}|$ in our metal complex will also be about 12 Hz. Likewise ${}^2J^M{}_{PP}$ is taken to be the same as in the previous complexes.[16] It is quite apparent that ring strain would have an effect on these values but at the moment no better assumptions are available. The results (Hz) given in Table V are good for Cr (obsd, 23; calcd, 29) and Mo (obsd, 15; calcd, 16) although poor for W (obsd, 21; calcd, 10). Additional work is needed to further substantiate and elucidate the additive coupling constant hypothesis proposed, but this work adequately demonstrates its plausibility.

J_{WP} values for the tungsten compounds $[Ph_2P(CH_2)_3PPhR]W(CO)_4$ all fall within the range of 216–222 Hz, with the diphenylphosphino group having a slightly larger value than the alkylphenylphosphino group. These compare with average values of about 200 and 228 Hz for $[Ph_2P(CH_2)_nPR^1R^2]W(CO)_4$, where $n = 1$ and 2, respectively. So far this trend, J_{MP}(5-membered ring) > J_{MP}(6-membered ring) > J_{MP}(4-membered ring), has been consistently observed. Previous examples for $[Ph_2P(CH_2)_nPPh_2]W(CO)_4$ where the values for $n = 2$, 3, and 1 are 231, 222, and 202 Hz, respectively;[6] for $[Ph_2P(CH_2)_nPPh_2]PtCl_2$ where the values for $n = 2$, 3, and 1 are 3618, 3420, and 3098 Hz, respectively;[7] and for $[Ph_2P(CH_2)_nPPh_2]PtMe_2$ where the values for $n = 2$, 3, and 1 are 1794, 1790, and 1434 Hz, respectively.[7] The considerably lower values for the four-membered chelate ring are undoubtedly due to ring strain.

The proton NMR results are only of moderate interest. The six methylene protons of the chelate backbone give a broad and complex multiplet which is unresolvable at 100 MHz with irradiation at the phosphorus frequencies. Only the chemical shifts and coupling constants for the methyl groups are recorded in the Experimental Section. The two methyl groups of the isopropyl compounds $[Ph_2P(CH_2)_3PPh(i\text{-}Pr)]M(CO)_4$ are diastereotopic and thus give rise to separate signals.[19] The resulting expected eight-line pattern often overlaps to give six lines of intensity 2:2:1:1:1:1. The assignments are given in the Experimental Section.

Table VI contains the carbonyl stretching frequencies for $[Ph_2P(CH_2)_3PPhR]M(CO)_4$. The four bands expected for this stereochemistry are present.[20]

In summary, nine group 6 metal carbonyl complexes of 1-(diphenylphosphino)-3-(alkylphenylphosphino)propane have been prepared and examined by ^{31}P NMR spectroscopy. The data along with the previous data from the analogues $[Ph_2P(CH_2)_2PR^1R^2]M(CO)_4$ and $[Ph_2PCH_2PR^1R^2]M(CO)_4$ have been used to demonstrate that the overall phosphorus–phosphorus coupling constants in these compounds can be separated into two components: transmission via the σ bonds in the ligand backbone and via the σ bonds through the metal center.

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Registry No. $L_ICr(CO)_4$, 62264-02-2; $L_IMo(CO)_4$, 62263-98-3; $L_IW(CO)_4$, 62263-97-2; $L_{II}Cr(CO)_4$, 62263-96-1; $L_{II}Mo(CO)_4$, 62263-95-0; $L_{II}W(CO)_4$, 62263-94-9; $L_{III}Cr(CO)_4$, 62263-93-8; $L_{III}Mo(CO)_4$, 62263-92-7; $L_{III}W(CO)_4$, 62263-91-6; L_IS_2, 62263-63-2; $L_{II}S_2$, 62263-62-1; $L_{III}S_2$, 62263-61-0; L_I, 57137-57-2; L_{II}, 57137-58-3; L_{III}, 57137-65-2; L, 6737-42-4; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

References and Notes

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(16) Ring strain, bond angle, and s-character differences in five- and six-membered rings will undoubtedly affect $^2J^M{}_{PP}$ somewhat, but the magnitude of coupling constants involved indicates that these differences are probably minor. Four-membered rings would be expected to have greater strain with the result that the additivity equation for the coupling constants would be less accurate.

(17) Apparently the tetrahedral PCP bond angle of the ligand precludes two large metal atoms to be simultaneously bound, one to each phosphorus donor. This has been noted previously [R. L. Keiter and D. P. Shah, *Inorg. Chem.*, **11**, 191 (1972); R. L. Keiter and D. P. Shah, private communication] in the case of $Ph_2PCH_2PPh_2$ and the $W(CO)_5$ group.

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Reactions of Metal Carbonyl Complexes. 10.[1] Selenocarbonyl Complexes of Chromium(0), Manganese(I), and Rhenium(I)[2]

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Carbon diselenide reacts in the presence of PPh_3 with $(\eta^5\text{-}C_5H_4R)M(CO)_2(THF)$ (M = Mn, R = H, Me; M = Re, R = H) or $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(THF)$ to give the new selenocarbonyl complexes, $(\eta^5\text{-}C_5H_4R)M(CO)_2(CSe)$ and $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(CSe)$, and PPh_3Se. The spectroscopic properties (IR and ^{1}H NMR) of these complexes indicate that CSe is a better net electron-withdrawing (σ-donor + π-acceptor) group than both CO and CS.

Unlike CO, the related CS and CSe diatomic molecules are extremely unstable even at very low temperatures. Carbon monosulfide polymerizes, often explosively, above −160 °C,[4] while CSe has thus far eluded isolation,[5] although some data have been reported for its electronic spectrum.[6] Over the past 10 years, there have been numerous examples of CS stabilization by coordination to transition metals and thiocarbonyl complexes have been synthesized for all of the group 6B, 7B, and 8 metals with the exception of technetium and palladium.[7,8] Our research in this field has been concerned chiefly with the synthesis of complexes such as $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ by the reactions of labile intermediate complexes with CS_2/PPh_3 (eq 1).[1,9]

$$\begin{aligned}&(\eta^5\text{-}C_5H_5)M(CO)_2L + CS_2 + PPh_3\\&\quad\rightarrow(\eta^5\text{-}C_5H_5)M(CO)_2(CS) + PPh_3S + L \qquad (1)\\&\qquad M = Mn, Re;\ L = C_8H_{14}, THF\end{aligned}$$

We report here the extension of reaction 1 to the formation of the first examples of transition metal selenocarbonyl complexes using CSe_2/PPh_3 as the in situ source of CSe. It is evident that many more selenocarbonyls will probably be prepared in the near future because, shortly following our initial communication on this work,[10] Clark et al. reported briefly on the synthesis of $RuX_2(CO)(CSe)(PPh_3)_2$ [X_2 = Cl_2, Br_2, I(OH)] and also described the x-ray structure of the dichloro derivative.[11]

Experimental Section

The manganese complexes $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ (R = H, Me) were generous gifts from the Ethyl Corp., New York, N.Y. The other starting materials were prepared by the literature methods indicated: $(\eta^5\text{-}C_5H_5)Re(CO)_3$,[12] $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_3$.[13] Triphenylphosphine (Aldrich Chemical Co.) was used without further purification. Carbon diselenide was purchased from Strem Chemicals Inc., Danvers, Mass. All solvents were distilled under nitrogen prior to use.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory Inc., Woodside, N.Y. Melting points were taken on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded as described previously (accuracy ±1 cm^{-1}).[1] Mass spectra were obtained at 50–150 °C on an AEI-MS902 spectrometer operating at 70 eV. ^{1}H NMR spectra were measured at ~35 °C