^{13}C-and ^{31}P-NMR Study of Tetracarbonylbis(diphenylphosphino)alkanemetal(0) Complexes of The Group 6 Elements

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Tetracarbonylbis(diphenylphosphino)alkanemetal(0) complexes of the general formula $M(CO)_4[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]$ (M: Cr, Mo, W; n: 1, 2, 3) were synthesized from the reaction of $M(CO)_4(\eta^{2:2}$-1,5-cyclooctadiene) with the appropriate ligand and characterized by means of IR and NMR (^{13}C and ^{31}P) spectroscopy. Spectroscopic data shows that two phosphorus atoms in the complexes are identical and occupy two *cis*-coordiantion sites in a *pseudo*-octahedral coordination sphere of the metal. The comparative study of the coordination shift and the ^{31}P-^{13}C coupling constant reveals that two carbonyl groups *trans* to one of two phosphorus atoms in the diphosphine ligand are shifted toward the lower magnetic field more than those which are *cis* to both phosphorus atoms. This is ascribed to the fact that two multiface ligands such as carbonyl or phosphine compete for the use of metal d_π-orbitals more strongly when they are *trans* to each other.

Key words: Chromium, Molybdenum, Tungsten, Carbonyl, Diphosphine, NMR

Introduction

Molecules containing two tertiary phosphorus atoms linked by a flexible hydrocarbon chain coordinate the transition metals usually as a bidentate ligand[1] or rarely as a monodentate ligand.[2] More rarely, they bridge two transition metal atoms.[3] Well known diphosphines include bis(diphenylphosphino)methane (DPPM), 1,2-bis(diphenylphosphino)ethane (DPPE), and 1,3-bis(diphenylphosphino)-propane (DPPP), which are capable of chelating a wide range of metal substrates to yield complexes with four, five or six membered rings, respectively.[4] In the case of Group 6 metal carbonyls, the chelation product is usually cisM(CO$_4$(L-L), where L-L represents the chelating diphosphine ligand. Synthesis and spectroscopic study of the complexes in which the L-L ligand serves as bridge between two Group 6 metals have been reported recently[3c]. cis-M(CO)$_4$(L-L) complexes of group 6 metals are known for L-L = DPPM and DPPE, and have been studied by ^{31}P-NMR, IR and UV-Vis spectroscopy.[5] There exists also one X-ray structure determination of Mo(CO)$_4$(DPPM).[6] However, ^{13}C-NMR spectral data of such complexes have been given for only a few examples in the literature.[7] Here we report a systematic ^{13}C-and ^{31}P-NMR spectroscopic study on a

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series of the $M(CO)_4(L\text{-}L)$ complexes which can be synthesized in high yields by the following substitution reaction:

$M(CO)_4(\eta^{2:2}\text{-1,5-cyclooctadiene}) + L\text{-}L \xrightarrow{\Delta} M(CO)_4(L\text{-}L) + 1,5\text{-cyclooctadiene}$
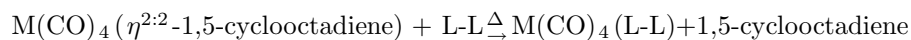
L-L:	M:	Cr	Mo	W
DPPM: bis(diphenylphosphino)methane		**1a**	**2a**	**3a**
DPPE: 1,2-bis(diphenylphosphino)ethane		**1b**	**2b**	**3b**
DPPP: 1,3-bis(diphenylphosphino)propane		**1c**	**2c**	**3c**

All the complexes were isolated and purified by recrystallization from dichloromethane/n-hexane solution at 223 K, and characterized by IR, ³¹P-, and ¹³C-NMR spectroscopy.

Experimental

All reactions and manipulations involving the metal carbonyl complexes were carried out either in a vacuum or under a dry and deoxygenated nitrogen atmosphere by using Schlenk techniques. Hexacarbonylchromium(0), hexacarbonylmolybdenum(0), hexacarbonyltungsten(0), bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 1,5-cyclooctadiene (COD), *n*-hexane, *n*-heptane, *iso*-octane, and dichloromethane were purchased from Aldrich Chemie, Germany, and used without any further purification, with the exception of solvents. Solvents were distilled after refluxing over metallic sodium or diphosphorus pentoxide under nitrogen for three to four days and stored until use. The photochemical reactions and other treatment of organometallic compounds such as purification and crystallization were followed by IR spectra taken at appropriate time intervals.

NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.132 MHz for ¹H, 161.975 MHz for ³¹P, and 100.612 MHz for ¹³C). TMS was used as the internal reference for both ¹H- and ¹³C-NMR chemical shifts, and 85% orthophoshoric acid in a capillary tube was used as the external reference for the ³¹P-NMR chemical shifts. Infrared spectra were recorded from *n*-hexane solution on a Perkin-Elmer 1430 or PC 16 FT-IR Spectrophotometer. Mass spectra were taken on a Varian MAT 311 instrument. Photochemical reactions were carried out in an irradiation apparatus with a Hanau TQ 150 high-pressure mercury lamp.

$M(CO)_4(\eta^{2:2}\text{-1,5-cyclooctadiene})$ (M: Cr, Mo, W) were prepared thermally or photochemically according to the procedures described in literature.[8]
$M(CO)_4(L\text{-}L)$ (M:Cr, Mo, W; L-L: DPPM, DPPE, DPPP)

To a solution of about 1 g of $M(CO)_4(\eta^{2:2}\text{-1,5-cyclooctadiene})$ in 20 ml n-hexane, a stoichiometric amount of bis(diphenylphophino)alkane ligand is added at room temperature. The mixture is stirred for one night at room temperature. The pale yellow reaction product is barely soluble in n-hexane, and therefore precipitates as the reaction proceeds. After evaporation of the volatiles, the residue is dissolved in a minimum amount of n-hexane: dichloromethane(5:1) and left to stand for one day for crystallization at 223 K. The solvent was decanted and crystals were dried in vacuo. All of the complexes were characterized by IR, ¹³C-, ³¹P-NMR spectroscopy.

Results and Discussion

The reaction of bis(diphenylphosphino)alkane, L-L, with an equimolar amount of $M(CO)_4(\eta^{2:2}\text{-1,5-cyclooctadiene})$ (M: Cr, Mo, W) yields the complexes of the type $M(CO)_4(L\text{-}L)$ in which the L-L ligand chelates

the transition metal atom. The IR-spectra of the complexes, **1a-3c,** show four absorption bands (Table 1) in the CO-setretching region, indicating a *cis* arrangement of four CO groups in the pseudo-octahedral coordination sphere of the metal. Thus the $M(CO)_4$-unit in the complexes has a local C_{2v}-symmetry with general CO vibrational modes of $2A_1+B_1+B_2$.[9] Complexes **2c** and **3c** yield only three IR absorption bands in the region of CO stretching vibrations, indicating that two of four bands are overlapping for these two compounds.

Table 1. The CO stretching frequencies (cm^{-1}) for the complexes in cyclohexane.

Complex	$A_{1(2)}$	$A_{1(1)}$	B_1	B_2
1a	2012	1922	1903	1891
1b	2012	1930	1901	1890
1c	2012	1923	1902	1889
2a	2020	1929	1917	1897
2b	2017	1928	1908	1897
2c	2023	1936	1908	
3a	2015	1935	1907	1980
3b	2015	1930	1883	
3c	2016	1933	1901	1888

The ^{13}C-{^{1}H}-NMR spectra of the complexes (Table 2) exhibit two signals of the relative intensities 1:1 for the CO ligands, providing additional evidence for the existence of $M(CO)_4$-unit with a local C_{2v} symmetry in the complex as elucidated from the IR-observation. The ^{31}P-{^{1}H}-NMR spectra (Table 3) exhibit only one highly down-field shifted signal for the complexes. This indicates that both of the phosphorus atoms of the bis(diphenylphosphino)alkane ligand are coordinated to the transition metal, and furthermore that the two phosphorus atoms are still equivalent. [13]P-{^{1}H}-NMR data provide additional evidence for the symmmetric coordination of the L-L ligand. We will now discuss the spectral data in more detail with the aim of delineating the bonding properties.

Table 2. The ^{13}C-NMR chemical shifts(δ ppm, ref.TMS) and [31]P-^{13}C coupling constants (Hz given in parenthesis) of the complexes in $CDCI_3$.

Comp	CO_{trans}	CO_{cis}	CO_2	i	o	m	p
				C_6H_5			
1a	229.38(19.7)	222.32(25.6)	47.70(36)	136.52(36)	131.20(12)	128.72(9.6)	130.09
2a	218.85(14.6)	210.48(17.5)	49.00(38)	136.21(37)	131.60(13.8)	128.70(9.8)	130.17
3a	210.30(14.7)	202.80(13.6)	51.69(47)	135.74(43)	131.81(13.1)	128.74(7.0)	130.81
1b	228.95(17.6)	220.03(27.1)	28.47(40)	136.83(35)	131.16(10.2)	128.62(7.2)	129.71
2b	217.85(9.0+25.5)	209.76(17.4)	28.11(40)	136.38(33)	131.37(12.8)	128.48(9.4)	129.72
3b	208.08(7.4+25.1)	201.18(13.6)	28.65(41)	136.12(35)	131.46(12.4)	128.36(8.2)	129.86
1c	225.98(18.8)	221.60(27.3)	30.69(23.1) 22.49(7)	137.76(36)	131.78(10.3)	128.31(8.5)	129.71
2c	214.92(14.6)	210.48(17.1)	31.36(22.1) 22.49(7)	137.62(34)	131.84(11.9)	128.31(9.4)	129.41
3c	205.97(15.3)	203.06(14.2)	31.13(23.2) 22.52(7)	137.16(40)	131.92(11.5)	128.34(9.4)	129.65

Table 3. ^{31}P-NMR chemical shifts (δ ppm, rel. to H_3PO_4), coordination shift ($\Delta\delta$ ppm) and ^{183}W-^{31}P coupling constants (Hz) of the complexes in $CDCl_3$.

Compound	Nr.	δ(ppm)	$\Delta\delta$(ppm)	J(^{183}W-^{31}P)(Hz)
DPPM	**a**	-31.2		
DPPE	**b**	-22.0		
DPPP	**c**	-26.7		
$Cr(CO)_4$(DPPM)	**1a**	26.63	57.8	
$Mo(CO)_4$(DPPM)	**2a**	2.01	33.2	
$W(CO)_4$(DPPM)	**3a**	-23.06	8.1	202
$Cr(CO)_4$(DPPE)	**1b**	80.01	102	
$Mo(CO)_4$(DPPE)	**2b**	55.27	77.3	
$W(CO)_4$(DPPE)	**3b**	41.49	63.5	230
$Cr(CO)_4$(DPPP)	**1c**	42.37	69.1	
$Mo(CO)_4$(DPPP)	**2c**	25.89	52.6	
$W(CO)_4$(DPPP)	**3c**	1.11	27.8	222

Inspection of the ^{31}P-NMR data in Table 3 shows a metal dependence of the phosphorus coordination shif in the series of complexes for each L-L ligand. The phosphorus coordination shift of the chelate lignad decreases on passing from chromium through tungsten, as observed in similar carbonyl-phosphine-metal(0) complexes.[10] This up-field shift of the phosphorus resonance signal by about 20 ppm upon changing the metal from chromium to molybdenum or from molybdenum to tungsten has been explained as a neighbour anisotropy effect.[11] The ^{31}P-{^{1}H}-NMR signals of the tungsten complexes are composed of a very intense singlet accompanied by the tungsten satellites.[12]

The ^{13}C-NMR signals of the carboyl ligands in the complexes appear generally as a triplet because of the similar ^{31}P-^{13}C coupling of the carbonyl carbon to two phosphorus atoms. In line with the metal dependence of the ^{31}P-NMR chemical shift, one observes the largest downfield shift in the ^{13}C-NMR signals of the carbonyl groups for the chromium upon phosphine substitution. This reflects the existence of strongest P→M σ-donation and M→CO π-bonding in the chromium complexes.

The replacement of some CO groups in metal-carbonyls by a ligand which is a better σ-donor but a weaker π-acceptor than carbon monoxide leads to a deshielding of the carbon atom in the remaining CO-groups, as observed for similar complexes.[13] This deshielding reflects the enhancement of the metal-CO π back-bonding upon CO-substitution with a ligand which is a stronger σ-donor and a weaker π-acceptor than carbon monoxide. The fact that the carbonyl groups *trans* to the phosphine ligand show a larger down-field shift than the *cis* groups indicates that the deshielding effect is greatest for the *trans* ligand.[14] Carbon monoxide and phosphine are both two-face ligands possessing two π-orbitals available for the metal→ligand back-bonding. The replacement of CO by phosphine will strengthen the M-C bond for the remaining carbonyl ligands, because of the higher competitiveness of the carbon monoxide for the use of metal d_{π}-orbitals. However, the carbonyl groups *trans* to the phosphine ligand shows a larger downfield shift than the others in all complexes. This indicates that the effect of the phosphorus ligand on the carbonyl group is largest if they are *trans* to each other whereby they compete for the use of two metal d_{π}-orbitals.[15] However, they compete for the use of only one metal d_{π}-orbitals when they are *cis* to each other. Consequently, the chemical shift for carbonyl carbons *trans* to a phosphorus atom of the diphosphine ligand is affected more and shifted toward a lower magnetic field than that of CO groups *cis* to the diphosphine ligand. This effect is also visible in the ^{31}P-^{13}C coupling constants of te carbonyl ligands. The *trans*-coupling is greater than

the *cis*-one (Table 2). The stronger *trans* ^{31}P-^{13}C coupling is attributed to the use of two metal dπ orbitals by two *trans*-ligands, while two *cis*-ligands share only one metal dπ orbital. In complexes **2b** and **3b**, the ^{13}C-NMR signal of the CO group *trans* to a P atom is not a triplet, but rather a doublet of a doublet. This indicates that the ^{31}P-^{13}C coupling constants of the equatorial corbons to phosphorus atoms are not equal (Table 2), as would be expected for all of the complexes. The small ^{31}P-^{13}C coupling constant may be assigned to the CO and the phosphorus atom which are *cis* to each other, while the large coupling constant may be assigned to those which are *trans* to each other. For the other complexes, the difference between these two ^{31}P-^{13}C coupling constants for the equatorial CO groups must be small or avaraged to an intermediate value.

The ^{13}C-NMR signals of the L-L carbon atoms also appear as a triplet similar to the carbonyl signals. The assignment of the ^{13}C-{^{1}H}-NMR signals to the corresponding carbon atoms of the L-L ligands is based on the consideration of the chemical shifts and the magnitude of the ^{31}P-^{13}C-coupling constants. The ^{13}C-NMR signals of the L-L ligands show coordination shifts which depend on the position of the corresponding carbon atom relative to the ligating phosphorus atoms (Table 2).[16]

Thus, the largest up-field shift is observed in the resonance signal of the *ipso*-carbon atom of the phenyl substituent upon cordination. This coordination shift decreases on going from *ipso*-through *para*-carbon. The shielding of the aromatic carbons is ascribed to an increase in the π-electron density in the ring upon coordination as the involvement of the phosphorus atom to the phenyl ring π-delocalization is reduced by th M$\rightarrow$P back bonding.[17] The L-L ligand must accept π-electron density from the filled metal d-orbitals into the empty d-orbitals on the phosphorus atoms. This additional electron density in the phosphorus d-orbitals can be pumped into the ring through the 2π-d$_\pi$ interactions. This enhanced delocalization results in an upfield shifts of the phenyl carbon atoms in the coordinated diphosphine.

Acknowledgment

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