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HETERONUCLEAR TRANSITION METAL COMPLEXES
II*. CHELATING DIPHOSPHINE AND DIARSINE PALLADIUM AND PLATINUM DI-μ-ORGANOTHIOTETRACARBONYLS OF GROUP VI, $L\text{-}LM'(SR)_2M(CO)_4$

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SUMMARY

Members of the series $L\text{-}LM'(SR)_2M(CO)_4$ [L–L = 1,2 bis(diphenylphosphino)ethane, *o*-phenylenebis(diethylarsine); M' = Pd, Pt; R = Me, Ph; M = Cr, Mo, W] have been prepared by ligand replacement reactions. The complexes, although highly stable as solids, decompose rapidly in solution. From their IR and diffuse reflectance electronic spectra there is evidence that the complexes $L\text{-}LM'(SR)_2$ behave simply as chelating disulphide ligands; in contrast to the complexes $(\pi\text{-}C_5H_5)_2Ti(SR)_2M(CO)_4$[1] there is no evidence for any metal–metal bonding.

INTRODUCTION

The scope of ligand replacement reactions has been extended to the preparation of heteronuclear transition metal complexes containing a Group VIII and a Group VI metal. These novel complexes (I) have the general formula $(L\text{-}L)M'(SR)_2M(CO)_4$ [L–L = 1,2-bis(diphenylphosphino)ethane, *o*-phenylenebis(diethylarsine); M' = Pd, Pt; R = Me, Ph; M = Cr, Mo, W].

In a previous paper[1] of this series we showed that it was possible to infer, from spectroscopic data, the presence of Ti–M σ-bonding in the complexes $(\pi\text{-}C_5H_5)_2Ti(SR)_2M(CO)_4$ (II) (R = Me, Ph; M' = Cr, Mo, W), which we regard as mesomeric between forms (IIa) and (IIb). In this paper we present similar data for complexes (I) and use them to compare and contrast metal–metal interactions in (I) and (II).

(*continued on p.* 126)

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* For Part I see ref. 1.

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TABLE 1

Complex	Analyses found (calcd.) (%)				M.p.[a] (°C)	$\nu(C{\equiv}O)$[b] in $CHCl_3$ soln.	$\bar{k}$[c]	Electronic spectra (diffuse reflectance) (cm^{-1})	Electronic spectra in $CHCl_3$ solution (cm^{-1}) (ε)	NMR[d] of S–CH_3 protons
	C	H	S	P						
$Ph_2PCH_2CH_2PPh_2Pd(SMe)_2Cr(CO)_4$	50.2	4.1	7.3	9.2	190[e]	1978, 1856[f],		22,500		
(nc)	(50.5)	(4.0)	(8.4)	(8.1)		1849, 1806				
$Ph_2PCH_2CH_2PPh_2Pd(SMe)_2Mo(CO)_4$	47.5	4.1			190–193	2003, 1843,	14.53	22,700		
(nc)	(47.6)	(3.8)				1863, 1823				
$Ph_2PCH_2CH_2PPh_2Pd(SMe)_2W(CO)_4$	42.7	3.8	7.0	6.4	161–164	1994, 1890,	14.40	22,200		
(nc)	(42.9)	(3.4)	(7.2)	(6.9)		1833[g]				
$Ph_2PCH_2CH_2PPh_2Pt(SMe)_2Cr(CO)_4$	45.9	3.9	7.4	7.9	120[e]	1994, 1884,	14.42	22,700		
(nc)	(45.1)	(3.5)	(7.5)	(7.3)		1861, 1817				
$Ph_2PCH_2CH_2PPh_2Pt(SMe)_2Mo(CO)_4$	43.5	3.6	6.3	7.4	160[e]	2005, 1893,	14.50	23,500		
(nc)	(42.9)	(3.4)	(7.2)	(6.9)		1860, 1817				
$Ph_2PCH_2CH_2PPh_2Pt(SMe)_2W(CO)_4$	39.2	2.9	6.1		170–174	1998, 1881,	14.38	24,100		
(nc)	(39.2)	(3.1)	(6.5)			1853, 1811				
$C_6H_4As_2Et_4Pd(SMe)_2Mo(CO)_4$	31.4	3.9			150[e]	2004, 1886,	14.41	23,000		
(nc)	(32.2)	(4.0)				1851, 1810				
$C_6H_4As_2Et_4Pd(SPh)_2Mo(CO)_4$	41.0	3.9			117–120	2008, 1894,	14.55	21,000		
(nc)	(41.3)	(3.9)				1864, 1821				
$Ph_2PCH_2CH_2PPh_2Pd(SMe)_2$	56.4	5.1	10.2	10.3	193–197			24,400	22,000(210)	7.98
(nc)	(56.2)	(5.2)	(10.6)	(10.3)				22,700	24,300(270) 29,700(11,700)	

$Ph_2PCH_2CH_2PPh_2Pd(SPh)_2$					210–215[h]				21,200(1,100) 29,800(12,200)	7.98
$Ph_2PCH_2CH_2PPh_2Pt(SMe)_2$	48.9	4.4	9.1	8.6	240–243			25,900	26,100(140)	7.88
(nc)	(48.9)	(4.4)	(9.3)	(9.0)					32,700(3,600)	
$Ph_2PCH_2CH_2PPh_2Pt(SPh)_2$	56.4	4.2			222–225				25,000(340)	
(nc)	(56.2)	(4.2)							32,600(6,400)	
$C_6H_4As_2Et_4Pd(SMe)_2$	35.4	5.8			151–153			22,800	22,700(300)	7.60
(nc)	(35.2)	(5.6)							28,900(3,600)	
$C_6H_4As_2Et_4Pd(SPh)_2$	46.9	5.3			165–168			22,500	21,600(1,400)	
(nc)	(47.0)	(5.1)							29,200(5,100)	
$C_6H_4As_2Et_4Pt(SMe)_2$	31.0	4.7			150–152				25,600[i]	7.40
(nc)	(31.1)	(4.8)							30,500(1,200)	
$MeSCH_2CH_2SMeCr(CO)_4$[j]					230	2020, 1914, 1848, 1869	14.98		26,300(400)	
$MeSCH_2CH_2SMeMo(CO)_4$[j]					148	2030, 1919, 1905, 1868	15.07		27,600(1,600)	
$MeSCH_2CH_2SMeW(CO)_4$[j]					160	2023, 1910, 1897, 1867	14.97		27,000(2,000)	
$PhSCH_2CH_2SPhMo(CO)_4$					120	2027, 1905, 1870	15.01		27,700(1,400)	

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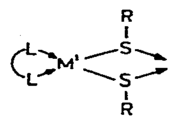
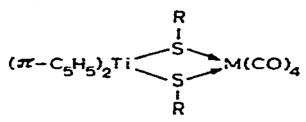
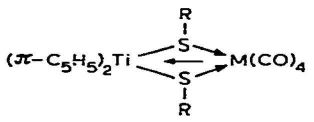
[a] Melt with decompn. unless otherwise indicated. [b] All peaks observed were strong. [c] See text. [d] In $CDCl_3$, τ values relative to internal TMS at 10.0 τ. [e] Decompn. without melting. [f] Nujol mull; complex too unstable in $CHCl_3$. [g] Accidental degeneracy of two of the stretching frequencies giving broad middle peak. [h] Ref. 2. [i] Exact position and intensity of peak not obtained because of proximity of higher energy peak at 30,500 cm^{-1}. [j] Ref. 6.



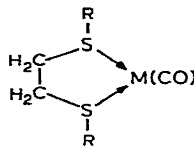
(I)



(IIa)



(IIb)



(III)

EXPERIMENTAL

Microanalyses (see Table 1) were carried out by Mr. C. E. O'Brien, Imperial Chemical Industries Ltd. IR spectra (4000–400 cm^{-1}) were recorded on a Perkin–Elmer 157 Grating Spectrophotometer calibrated with carbon monoxide. The diffuse reflectance visible-UV spectra were recorded on a Beckman DK-2A spectrophotometer using a lead sulphide cell as detector at wavelengths longer than 700 nm and a photomultiplier tube for shorter wavelengths.

All reactions were carried out in sodium dried, sulphur free toluene previously purged with nitrogen. The reaction mixtures were maintained under a positive pressure of nitrogen.

Preparation of L–LM′(SR)$_2$

Although several complexes of the general formula $L_2M'(SR)_2$ (L = arylphosphine; M′ = Ni, Pd; R = Et, Ph) have been prepared by the reaction of NaSR with the corresponding dichloride, $L_2M'Cl_2$, in ethanol[2], better results were obtained, at least for complexes containing chelating ligands, by treating a suspension of $L{-}LM'Cl_2$ in toluene with RSH in the presence of triethylamine. Using this route, yields of over 80% were obtained in all cases.

Preparation of bis(methylthio)[1,2-bis(diphenylphosphino)ethane]platinum(II), $Ph_2PCH_2CH_2PPh_2Pt(SMe)_2$. 2 g. of $Ph_2PCH_2CH_2PPh_2PtCl_2$ were stirred in 150 ml toluene in a flask fitted with a dry-ice condenser. The suspension was cooled to −78° using an acetone/dry-ice bath and 2 ml of methanethiol and 5 ml of triethylamine were added. The mixture was allowed to come to room temperature and stirred for 8 h. The dry-ice condenser was then removed to allow excess methanethiol to evaporate. The crude yellow product was filtered off, washed with cold water and ethanol and crystallised from a large volume of ethanol. The product was obtained as pale yellow crystals, m.p. 240–243° decompn.

The complexes described below were prepared in the same way.

Bis(methylthio)[1,2-bis(diphenylphosphino)ethane]palladium(II), $Ph_2PCH_2CH_2PPh_2Pd(SMe)_2$. Yellow crystals, m.p. 193–197° decompn.

Bis(phenylthio)[1,2-bis(diphenylphosphino)ethane]platinum(II), $Ph_2PCH_2CH_2PPh_2Pt(SPh)_2$. Yellow needles, m.p. 222–225° decompn.

Bis(methylthio)[o-phenylenebis(diethylarsine)]palladium(II), $C_6H_4(AsEt_2)_2Pd(SMe)_2$. Orange crystals, m.p. 151–153° decompn.

Bis(methylthio)[o-phenylenebis(diethylarsine)]platinum(II), $C_6H_4(AsEt_2)_2$-$Pt(SMe)_2$. Pale yellow crystals, m.p. 150–152° decompn.

Bis(phenylthio)[o-phenylenebis(diethylarsine)]palladium(II), $C_6H_4(AsEt_2)_2$-$Pd(SPh)_2$. Orange/red crystals, m.p. 165–168°.

The diarsine derivatives, being more soluble, were crystallised from toluene. No cooling or dry-ice condenser were required in the preparations of the phenylthio derivatives.

Preparation of L–LM′(SR)$_2$M(CO)$_4$

The heterodinuclear complexes were obtained by the reaction of equimolar amounts of L–LM′$(SR)_2$ and the corresponding *norbornadiene*-Group VI metal tetracarbonyl. The complexes thus prepared were found to be insoluble in most solvents and stable for only very short periods in such polar solvents such as methylene chloride or acetone. Thus, no suitable solvent for crystallisation was found, and the purity of the products was controlled by varying the reaction times.

Preparation of $Ph_2PCH_2CH_2PPh_2Pt(SMe)_2Mo(CO)_4$. A suspension of 0.50 g (0.73 mmole) of $Ph_2PCH_2CH_2PPh_2Pt(SMe)_2$ was stirred in 70 ml toluene with 0.22 g (0.73 mmole) of norbornadiene molybdenum tetracarbonyl for 48 h at room temperature. The light brown solid was filtered off, washed with toluene and pentane, and dried *in vacuo* at room temperature. The following complexes were prepared in the same way using similar quantities of reactants; reaction times are given.

$Ph_2PCH_2CH_2PPh_2Pd(SMe)_2Cr(CO)_4$.	46 *h* .
$Ph_2PCH_2CH_2PPh_2Pt(SMe)_2Cr(CO)_4$.	120 *h* .
$Ph_2PCH_2CH_2PPh_2Pd(SMe)_2Mo(CO)_4$.	30 *h* .
$Ph_2PCH_2CH_2PPh_2Pd(SMe)_2W(CO)_4$.	48 *h* .
$Ph_2PCH_2CH_2PPh_2Pt(SMe)_2W(CO)_4$.	60 *h* .
$C_6H_4(AsEt_2)_2Pd(SMe)_2Mo(CO)_4$.	2 *h* .
$C_6H_4(AsEt_2)_2Pd(SPh)_2Mo(CO)_4$.	4 *h* .

The much shorter reaction times required for the preparation of the diarsine complexes is probably due to the increased solubility of the starting material (L–L)-$M(SR)_2$ in toluene, as compared with the phosphine complexes.

The complexes $Ph_2PCH_2CH_2PPh_2M'(SPh)_2M(CO)_4$ (M′ = Pd, Pt; M = Cr, Mo, W) and $C_6H_4(AsEt)_2Pd(SR)_2M(CO)_4$ (R = Me, Ph; M = Cr, W) were not obtained pure because of extremely slow reactions and/or instability of the desired products.

Infrared spectra

The infrared spectra of the complexes were recorded using freshly prepared chloroform solutions. Peaks present in fresh solutions which decreased in intensity with time were assigned to the heterodinuclear species; those peaks which increased in intensity with time were assigned to decomposition products.

Because of this decomposition and the lack of a suitable solvent in which the complexes were stable, ^1H NMR spectra could not be obtained.

RESULTS AND DISCUSSION

The novel heterodinuclear complexes with analytical data, IR carbonyl stretching frequencies and mean force constants, and observed transitions in their electronic spectra are listed in Table 1 together with similar data on related complexes for comparison.

Infrared data

It has been shown[3] that the introduction of a silicon or tin atom into a chelating diphosphine or diarsine complexed to a metal carbonyl will lower the IR carbonyl stretch frequency. This effect is attributed to the decrease in electronegativity on going from carbon to silicon or tin making the phosphorus or arsenic atoms better electron donors. From similar arguments it is therefore to be expected that complexes (I) will have lower IR carbonyl stretching frequencies than complexes (III) (for given R). As can be seen from Table 1 both the IR carbonyl stretching frequencies and the stretching parameters derived from them* are lower in complexes (I) than in complexes (III).

The above argument assigns the observed lowering of the stretching frequencies and stretching parameters to stronger σ-donor (and/or weaker π acceptor) character of the sulphur atoms in (I) as compared with (III). Non-bonded repulsion between the *d*-electrons on M and M′ would also lead to increased M→CO π-donation, and hence may also be contributing to a lowering of the carbonyl stretching frequencies.

Although the electronegativities of Pd and Pt are similar on both the Pauling and the Allred–Rochow scales[4], the S-methyl protons in L–LPd(SMe)$_2$ resonate at slightly higher field than those in L–LPt(SMe)$_2$. One might therefore have suspected the former compounds to be better electron donors; but such effects, if present, are too small to affect the observed carbonyl frequencies.

Electronic spectra

The diffuse reflectance spectra of complexes (I) and the solution and diffuse reflectance spectra of L–LM′(SR)$_2$ are similar to the range which could be covered (14000–28000 cm^{-1}) by the diffuse reflectance technique. The low energy band (22000–25000 cm^{-1}) in the solution spectra of L–LM′(SR)$_2$ is assignable to a $d \rightarrow d$ transition in M′. (The higher energy band is presumably charge transfer.) We would assign the band observed in complexes (I), which occurs at similar energy to that observed in L–LM′(SR)$_2$, to a $d \rightarrow d$ transition in M′. It is not assigned to a transition involving M since the solution spectra of complexes (III) show no bands below 26000 cm^{-1}.

Since the lowering of the IR carbonyl stretching frequencies in complexes (I) as compared with (III) can be explained by electronegativity changes (or possibly to some extent by repulsion between M and M′) and the bands observed in the electronic spectra of (I) match those of (L–L)M′(SR)$_2$, we have no evidence to suggest dispersion of electron density on M. While there is evidence of a Ti–M bond in complexes (II) (IIa)[1] there is no reason to postulate an M–M′ bond in complexes (I).

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* For the method of determining the average CO force constant, $\bar{k}$, see ref. 1.

STRUCTURES AND BONDING. CONCLUSIONS

The $\mathrm{M}\begin{smallmatrix}\diagup\mathrm{B}\diagdown\\ \diagdown\mathrm{B}\diagup\end{smallmatrix}\mathrm{M}$ ring (where B is a bridging ligand) has been found to be planar in all transition metal complexes which do not contain a metal–metal bond[5]. The MBM angle is obtuse and the BMB angle is acute because of repulsive forces between the two metal atoms. The structures of complexes (I) will probably be of this type; the question of geometrical isomerism, as found in complexes (II)[1], cannot in this case be settled from the information available.

$\mathrm{L{-}LM'(SR)_2}$, like $(\pi\text{-}\mathrm{C_5H_5})_2\mathrm{Ti(SR)_2}$, contains a 16-electron central metal atom. There is therefore a theoretical possibility of an $\mathrm{M \rightarrow M'}$ bond. Inspection of the available orbitals shows that this would have to be a $dxz \rightarrow pz$ π-bond unsupported by any σ-bond; we find no evidence for this.

The IR and electronic spectra of the heteronuclear complexes can be explained by considering $\mathrm{L{-}LM'(SR)_2}$ as a chelating ligand, similar to $\mathrm{RSCH_2CH_2SR}$, in which the methylene carbon atoms have been replaced by a less electronegative element.

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