

### Preliminary communication

#### PREPARATION OF TERDENTATE COMPLEXES OF

4-CYCLOHEXYLPHOSPHORIN:  $\pi\text{-M}(\text{CO})_3\text{C}_{11}\text{H}_{15}\text{PM}'(\text{CO})_5$  ( $\text{M} = \text{Cr}, \text{Mo}; \text{M}' = \text{Cr}, \text{Mo}, \text{W}$ )

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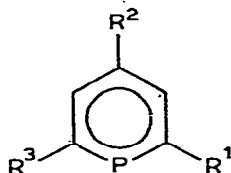
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#### Summary

The first examples of a  $\pi$ -bound aromatic heterocyclic ring in which the hetero atom is also  $\sigma$ -bonded to a second metal atom have been prepared.

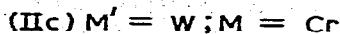
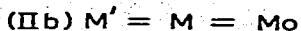
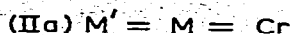
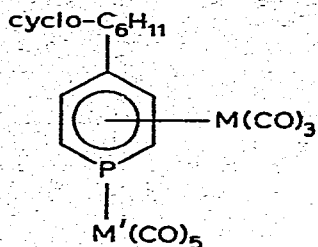
Since the synthesis of 2,4,6-triphenyl- $\lambda^3$ -phosphorin (Ia) [1] in 1966, a great deal of effort has been expended in developing routes to the preparation of other members of this family of compounds. Although there have been several investigations of Ia [2,3], the coordination chemistry of  $\lambda^3$ -phosphorins remains largely unexplored. Shortly after Märkl [4] described the synthesis of 4-cyclohexyl- $\lambda^3$ -phosphorin (Ib) we initiated a study of transition-metal-phosphorin complexes. We chose to investigate the reactions of Ib on the basis of its relative ease of preparation and to exclude the possibility of steric interference by groups in the 2 and 6 positions.



(Ia)  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{C}_6\text{H}_5$

(Ib)  $\text{R}^1 = \text{R}^3 = \text{H}; \text{R}^2 = \text{cyclo-C}_6\text{H}_{11}$

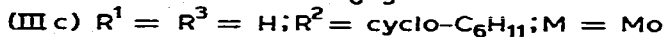
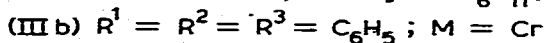
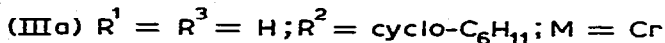
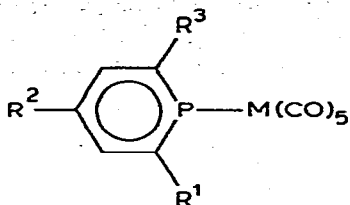
During our study of the reactions between the Group VIB carbonyls and Ib, we prepared the unique compounds IIa—IIc in which the phosphorin is bound to two metal atoms. We believe these compounds to be the first examples of a  $\pi$ -bound aromatic heterocyclic ring in which the hetero atom is also  $\sigma$ -bonded to a second metal atom. A  $\text{M}(\text{CO})_3$  group is  $\pi$ -bonded to the aromatic phosphorin ring and the phosphorus atom is also  $\sigma$ -bonded to a  $\text{M}(\text{CO})_5$  moiety.



Complexes IIa and IIb can be prepared by heating the appropriate metal hexacarbonyl with Ib in refluxing *n*-butyl ether for one hour under an inert atmosphere. Following solvent removal and extraction of the residue with pentane, the compounds were purified by column chromatography on fluorosil and the light orange to yellow crystalline products isolated from a chilled pentane solution.

The structures of the compounds were deduced from elemental analysis and infrared and mass spectral data. Analysis: IIa: Found: C, 45.2, H, 3.0, P, 6.5.  $\text{C}_{19}\text{H}_{15}\text{Cr}_2\text{O}_8\text{P}$  calcd., C, 45.1, H, 3.0, P, 6.1%. IIb: Found, C, 38.6, H, 2.6, P, 5.3,  $\text{C}_{19}\text{H}_{15}\text{Mo}_2\text{O}_8\text{P}$  calcd., C, 38.4, H, 2.6, P, 5.2%.

Ligands Ia and Ib have previously been reported by Nöth [2] and Sears [5], respectively, to form both  $\pi$  and  $\sigma$  bound complexes with chromium and molybdenum carbonyls. Examination of the infrared data in Table 1 clearly shows that complexes IIa and IIb exhibit absorptions characteristic of  $\text{M}(\text{CO})_3$  and  $\text{M}(\text{CO})_5$  groups. The carbonyl stretching frequencies for the  $\text{M}(\text{CO})_5$  in IIa and IIb are shifted to higher wavenumbers relative to IIIa,b and IIIc,d respectively.



Similarly the  $\text{M}(\text{CO})_5$  absorptions of IIa and IIb are shifted up relative to IV. The observed trend of the CO stretching frequencies is anticipated on the basis of the expected decrease in electron density of the ligand caused by simultaneous coordination to two metal atoms.

The mass spectrum of IIa exhibits a peak for the molecular ion at  $m/e$  506, followed by peaks for the successive loss of the eight CO groups and finally the loss of the two Cr atoms and the normal fragmentation pattern of the ligand.

TABLE I

## PHYSICAL PROPERTIES OF 4-CYCLOHEXYLPHOSPHORIN COMPLEXES

Complex	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )	M.p. ( $^{\circ}\text{C}$ )	Color
IIa	2077 w 1991 s 1966 vs 1935 s	135–137	orange
IIb	2085 w 1998 s 1970 vs 1940 s	116–118	yellow
$[\sigma\text{-L}'\text{Cr}(\text{CO})_5]$ (IIIa)	2071 w 1961 vs	74–76	light orange
$[\sigma\text{-LCr}(\text{CO})_5]$ (IIIb) [2]	2072 1959	140–141	orange
$[\sigma\text{-L}'\text{Mo}(\text{CO})_5]$ (IIIc)	2078 w 1964 vs	86–89	yellow
$[\sigma\text{-LMo}(\text{CO})_5]$ (IIId) [2]	2076 1960	137–139	yellow
$[\pi\text{-LCr}(\text{CO})_3]$ (IV) [2]	1987 s 1917 s		

<sup>a</sup>L = Ia; L' = Ib

The molecular ion for IIb could not be observed. The initial fragmentation is to  $\text{Mo}(\text{CO})_3^+$  and  $\text{C}_{11}\text{H}_{15}\text{PMo}(\text{CO})_5^+$ . The latter species exhibits a fragmentation pattern identical to that of IIIc. This mode of fragmentation for IIb is consistent with the lesser tendency of molybdenum relative to chromium to form  $\pi$ -complexes.

In the  $^1\text{H}$  NMR spectrum of the complexes (IIa and IIb in  $\text{CDCl}_3$ ), compared with the free ligand, there is a distinct upfield chemical shift which is characteristic of  $\pi$ -bonded aromatic compounds.

Complex IIc is obtained as a mixture with IIa when  $\sigma\text{-C}_{11}\text{H}_{15}\text{PW}(\text{CO})_5$  is heated with  $\text{Cr}(\text{CO})_6$  in di-*n*-butyl ether. Similar mixtures also result when  $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$  or  $\text{C}_7\text{H}_5\text{Cr}(\text{CO})_3$  are substituted for  $\text{Cr}(\text{CO})_6$ . Attempts to isolate pure IIc have been unsuccessful to date. Its existence is based on infrared and mass spectral data. The mass spectrum unequivocally demonstrates its existence with the observation of the molecular ion ( $m/e$ , 638), systematic loss of the eight CO groups, followed by loss of chromium, then tungsten and the normal fragmentation of the ligand.

It is interesting to note that Ib readily forms a variety of stable transition metal complexes [5]. Theoretical calculations [6–8] employing the CNDO/2 method predict the parent phosphorin (I,  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$ ) to have an aqueous  $pK_a$  of  $-10$ . Solutions of Ia with strong acids (e.g.,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$ ) do not show any evidence for the formation of a phosphorinium ion [6–8]. Thus, one might anticipate phosphorins to be relatively poor ligands. However, hydrogen bonding studies indicate the basicity of Ib to be intermediate between that of tri-*para*-methoxyphenylphosphine and tri-*para*-methylphenylphosphine [9]. The results of the hydrogen bonding studies appear more consistent with the ability of Ib to form complexes.

## Acknowledgements

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