Journal of Organometallic Chemistry, 162 (1978) C19—C22

Preliminary communication

NEW IMINE-PHOSPHINE CHELATING AGENTS AND THEIR MOLYBDENUM(O) DERIVATIVES

THOMAS B. RAUCHFUSS
School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801 (U.S.A.)

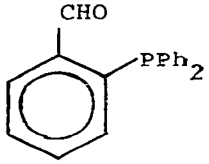
(Received August 8th, 1978)

Summary

The aldehyde o-$Ph_2PC_6H_4CHO$ condenses with a variety of functionalized amines to afford several new ligands which form stable mono- and bimetallic complexes with molybdenum(O).

---

o-Diphenylphosphinobenzaldehyde[1] **1** is a potentially versatile precursor to a variety of ligands via oxidation/reduction and nucleophilic additions. In this report, we



1

describe several iminophosphines derived from **1** and their molybdenum carbonyl derivatives.[2]

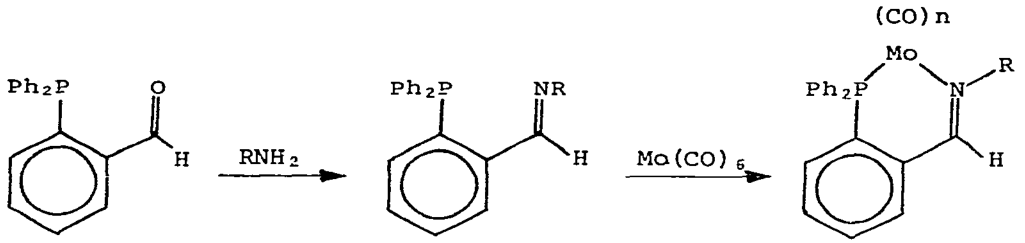
Condensation of the yellow aldehyde, **1**, with alkyl and aryl amines in refluxing ethanol affords the phosphine-imine chelating agents in high yield (Figure 1). The ligands with one exception were obtained as pale yellow oils which were identified by their spectroscopic properties (Table 1). The p-methoxyaniline derivative was isolated as straw needles and was spectroscopically similar to the other more flexible

Table 1

Selected Spectroscopic Data for New Ligands and Complexes

Compound	IR (cm^{-1})		^1H nmr[b]	
	ν_{CO}[a]	ν_{CN}	$\tau_{CH=N}$	Other
$p\text{-}MeOC_6H_4N{=}P$		1630[c]	8.83	3.53 (s, Me)
$Mo(p\text{-}MeOC_6H_4N{=}P)(CO)_4$	2023, 1910, 1864		8.20	3.73 (s, Me)
Allyl N=P		1640[d]	8.83	5.50-6.0 (m, -CH=)
$Mo(Allyl\ N{=}P)(CO)_4$	2022, 1904, 1861		8.25	5.35-5.78 (m, -CH=)
$Mo(2\text{-}pyCH_2N{=}P)(CO)_3$[e]	1922, 1814, 1798			
$CH_3SCH_2CH_2N{=}P$		1640[d]	8.80	1.98 (s, Me)
$Mo(CH_3SCH_2CH_2N{=}P)(CO)_3$	1929, 1812-1806 (br)		8.83	2.60 (s, Me)
$Mo_2(m\text{-}PDA{=}P_2)(CO)_8$[e]	2022, 1910, 1848		8.23	
$p\text{-}PDA{=}P_2$		1610[c]	8.96	
$Mo_2(p\text{-}PDA{=}P_2)(CO)_8$	2022, 1905, 1846			

a, in CH_2Cl_2 solution; b, in $CDCl_3$; c, Nujol mull; d, neat; e, the free ligand was not isolated.



Amine	Imine	Mo Complex
$CH_3OC_6H_4NH_2$	p-$MeOC_6H_4N$=P	Mo(p-MeC_6H_4N=P)$(CO)_4$
CH_2=$CH_2CH_2NH_2$	Allyl N=P	Mo(Allyl N=P)$(CO)_4$
2-$pyCH_2NH_2$	2-$pyCH_2N$=P	Mo(2-py-CH_2N=P)$(CO)_3$
$CH_2SCH_2CH_2NH_2$	$CH_3SCH_2CH_2N$=P	Mo($MeSCH_2CH_2N$=P)$(CO)_3$

Figure 1. Syntheses of mononuclear phosphine-imine complexes.

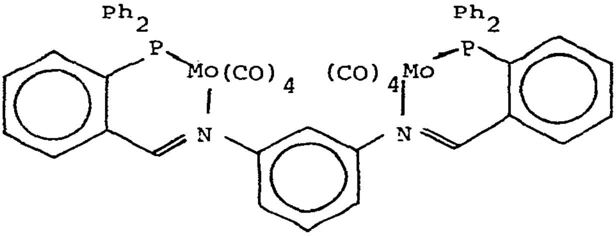
imines in addition to giving excellent elemental analyses.*

These imines react in boiling heptane with $Mo(CO)_6$ to yield orange and red di- and trisubstituted complexes respectively.[3] The molybdenum(O) derivatives are all highly crystalline, air stable, and chromatographically homogeneous. Both p-$MeOC_6H_4N$=P and allyl N=P function as bidentate ligands; attempts to replace a CO by the olefin in the tetracarbonyl complex of the allyl ligand photochemically or thermally were not successful. The pyridine chelating agent does bind the molybdenum in a tridentate manner and the similarity of its IR spectrum to other (N-N-P) $Mo(CO)_3$ complexes[3] suggests the facial geometry for this complex. The thioether $MeSCH_2CH_2N$=P represents a *unique* example of a P-N-S chelating agent and its molybdenum tricarbonyl derivative also adopts the all-*cis* geometry. The 90 MHz ^1H nmr spectrum of this compound in $CDCl_3$ shows a substantial downfield shift for the S-methyl relative to the free ligand (Table 1) in addition to an apparent AA'BB' pattern for the ethylene protons. This complex together with detailed spectroscopic and structural data for the complex of the ethylenediimine derivative of **1** will be described in a future publication.

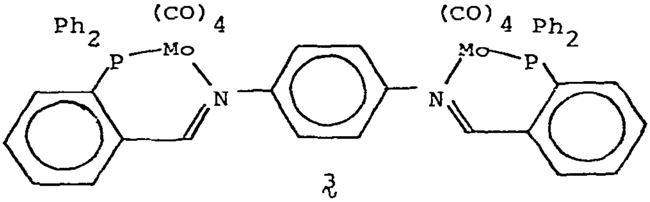
---

*The crystalline ligands and all metal complexes gave excellent elemental analyses which were presented to the referees.

The m- and p-phenylenediamines also condense with 1 to afford the novel binucleating ligands abbreviated m-PDA=P_2 and p-PDA=P_2 respectively. The meta isomer being an oil, the crude ligand was reacted directly with $Mo(CO)_6$ in chlorobenzene (110°, 12 hr) to afford orange crystals of the bimetallic complex (m-PPA=P_2)$Mo_2(CO)_8$ 2. The ligand p-PDA=P_2, on the other hand, was easily isolated as bright yellow moderately soluble crystals, and reacts with $Mo(CO)_6$ under similar conditions to yield the poorly soluble (p-PDA=P_2)$Mo_2(CO)_8$ 3. The IR spectra of both binuclear complexes closely resemble those obtained for the mononuclear complexes of the bidentate ligands (Table 1). The electrochemical properties of these compounds are under investigation.



2



3

References

1 G. P. Schiemenz and H. Kaack, Liebigs Ann. Chem. (1973) 1480.

2 For other imino phosphine complexes see: T. D. DuBois, Inorg. Chem., 11 (1972) 718; J. Riker-Nappier and D. W. Meek, Chem. Commun. (1974) 442; J. de O. Cabral, M. F. Cabral, M. G. B. Drew, S. M. Nelson, and A. Rogers, Inorg. Chim. Acta, 25 (1977) L77.

3 L. W. Houk and G. R. Dobson, Inorg. Chem., 5 (1966) 2119.