

MOLYBDENUM CARBONYL COMPLEXES OF (DIALKYLAMINO)- DIPHENYLPHOSPHINES (R_2NPPH_2)

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SUMMARY

Reactions of (dialkylamino)diphenylphosphines (R_2NPPH_2 ; $R = Me, Et, Pr, Bu$) with $Mo(CO)_6$ and $(C_7H_8)Mo(CO)_4$ have been studied, and the following complexes prepared: $(R_2NPPH_2)Mo(CO)_5$ ($R = Et, Pr, Bu$); *cis*- and *trans*- $(R_2NPPH_2)_2Mo(CO)_4$ ($R = Me, Et, Pr, Bu$). IR, NMR and mass spectral data for these complexes are reported. Attempts to prepare dinuclear molybdenum complexes with both phosphorus and nitrogen as bridging ligand atoms yielded only phosphorus-bridged derivatives.

INTRODUCTION

Studies of the synthesis and reactivity of dinuclear molybdenum carbonyl complexes have included the reactions of diphosphines with molybdenum hexacarbonyl to give μ -diphosphido derivatives¹⁻³. Earlier work⁴ had shown that $[\pi-C_5H_5Mo(CO)_3]_2$ forms phosphido- and hydrido-bridged species with tetramethyldiphosphine. The present work was intended to extend such reaction schemes to the preparation of dinuclear complexes containing both phosphorus and nitrogen as bridging ligands by using (dialkylamino)diphenylphosphines. There are many examples of reactions between metal carbonyls and tri-covalent phosphorus derivatives containing P-C, P-O, P-S and P-halogen bonds⁵, but relatively few reports of P-N derivatives⁶⁻¹³.

EXPERIMENTAL

The ligands R_2NPPH_2 ($R = Me, Et, Pr, Bu$) were prepared by reaction of R_2NH with Ph_2PCl in 2/1 molar amounts in toluene at 0° following the procedure of Payne *et al.*¹⁴ Filtration, to remove amine hydrochloride, followed by distillation afforded pure samples of the aminophosphines, which were, except for Me_2NPPH_2 , liquids at room temperature. They undergo slow atmospheric oxidation.

Reaction of R_2NPPH_2 ($R = Pr, Bu$) with $Mo(CO)_6$ in 1/1 molar amounts in

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TABLE I

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR $(R_2NPPH_2)Mo(CO)_5$ AND $(R_2NPPH_2)_2Mo(CO)_4$

Compound	Yield ^a (%)	M.p. ^b (°C)	Dipole moment ^c (D)	Analysis found (calcd.) (%)				
				C	H	N	P	Mo
<i>Cis</i> -(Me ₂ NPPH ₂) ₂ Mo(CO) ₄	50	154–158	6.21	58.2 (57.7)	4.8 (4.8)	4.2 (4.2)	8.6 (9.3)	14.4 (14.3)
<i>Trans</i> -(Me ₂ NPPH ₂) ₂ Mo(CO) ₄	32	169–173	2.29	57.7 (57.7)	4.8 (4.8)	4.1 (4.2)	8.1 (9.3)	13.6 (14.3)
(Et ₂ NPPH ₂)Mo(CO) ₅	25	68–71	4.27	50.6 (51.1)	4.0 (4.1)	2.9 (2.8)	7.0 (6.3)	18.2 (19.4)
<i>Cis</i> -(Et ₂ NPPH ₂) ₂ Mo(CO) ₄	64	150–154	6.64	60.1 (59.8)	5.6 (5.6)	4.0 (3.9)	8.2 (8.6)	13.2 (13.3)
<i>Trans</i> -(Et ₂ NPPH ₂) ₂ Mo(CO) ₄	40	154–159	2.20	60.4 (59.8)	5.9 (5.6)	4.0 (3.9)	8.6 (8.6)	13.2 (13.3)
(Pr ₂ NPPH ₂)Mo(CO) ₅	33	122–125	5.54	52.7 (53.0)	4.9 (4.6)	2.9 (2.7)	6.1 (5.9)	18.5 (18.4)
<i>Cis</i> -(Pr ₂ NPPH ₂) ₂ Mo(CO) ₄	54	141–143	6.59	62.8 (61.7)	6.4 (6.2)	3.8 (3.6)	7.1 (7.9)	11.9 (12.3)
<i>Trans</i> -(Pr ₂ NPPH ₂) ₂ Mo(CO) ₄	35	150–154	2.70	61.9 (61.7)	6.5 (6.2)	3.4 (3.6)	7.9 (7.9)	11.8 (12.3)
(Bu ₂ NPPH ₂)Mo(CO) ₅	26	119–122	5.64	55.2 (54.6)	5.3 (5.1)	2.7 (2.6)	5.4 (5.6)	16.1 (17.5)
<i>Cis</i> -(Bu ₂ NPPH ₂) ₂ Mo(CO) ₄	43	116–119	5.37	63.5 (63.2)	6.9 (6.8)	3.4 (3.4)	7.6 (7.4)	11.6 (11.5)
<i>Trans</i> -(Bu ₂ NPPH ₂) ₂ Mo(CO) ₄	43	116–119	4.08	61.8 (63.2)	6.5 (6.8)	3.3 (3.4)	6.6 (7.4)	10.9 (11.5)

^a Recrystallised product. ^b With decomposition. ^c Determined in benzene using a heterodyne beat capacity meter method¹.

TABLE 2

PROTON NMR SPECTRA OF (DIALKYLAMINO)DIPHENYLPHOSPHINE DERIVATIVES
Chemical shifts in τ values; J values in Hz.

Compound	C ₆ H ₅		CH ₃	α -CH ₂	β -CH ₂	γ -CH ₂	J (PH)	J (HH)
	<i>o</i>	<i>m+p</i>						
(CH ₃) ₂ NPPH ₂ ^a	2.55–2.75(m) ^c		7.40(d)				9.5	
<i>Cis</i> -L ₂ Mo(CO) ₄ ^b	2.65(m)		7.60(d)				11.0	
(C ₂ H ₅) ₂ NPPH ₂ ^a	2.50–2.80(bs)		8.9–9.2(t)	6.6–7.2(2oq)			9.9	7.3
LMo(CO) ₅ ^b	2.38(td)	2.58(m)	9.10(t)	7.8(dq)			11.0	7.3
<i>Cis</i> -L ₂ Mo(CO) ₄ ^b	2.37(m)	2.58(m)	9.20(t)	7.0(m)			^d	
(C ₃ H ₇) ₂ NPPH ₂ ^b	2.57(td)	2.72(m)	9.29(t)	7.06(q)	8.66(sex)		8.3	7.3
LMo(CO) ₅ ^b	2.40(t)	2.58(m)	9.28(t)	{ 6.95(t) 7.00(t)	8.72(m)		9.0	7.3
<i>Cis</i> -L ₂ Mo(CO) ₄ ^a	2.65(m)		9.36(t)	7.18(m)	8.74(m)		^d	
(C ₄ H ₉) ₂ NPPH ₂ ^b	2.60(td)	2.73(m)	9.23(t)	7.02(q)	8.70(m)	8.88(sex)	8.3	7.3
LMo(CO) ₅ ^b	2.42(t)	2.58(m)	9.23(t)	6.97(q)	8.86(m)		^d	
<i>Cis</i> -L ₂ Mo(CO) ₄ ^b	2.44(m)	2.65(m)	9.24(t)	{ 6.90(t) 7.15(t)	8.87(m)		^d	

^a Spectra taken in CDCl₃ at 60 MHz with TMS as internal standard. ^b Spectra taken in CDCl₃ at 220 MHz with TMS as internal standard. ^c Abbreviations used: bs = broad singlet, d = doublet, td = triplet of doublets, t = triplet, q = quartet, dq = double quartet, oq = overlapping quartet, sex = sextet, m = multiplet. ^d J (PH) indistinct.

TABLE 3

CARBONYL AND P-N STRETCHING FREQUENCIES, AND MASS SPECTRAL DATA FOR $(R_2NPPh_2)Mo(CO)_5$ AND $(R_2NPPh_2)_2Mo(CO)_4$

Complex	IR spectra		Mass spectra	
	$\nu(C\equiv O)^{a,b}$ (cm^{-1})	$\nu(P-N)$ (cm^{-1})	Parent ion ^d	Carbonyl loss
<i>Cis</i> -(Me ₂ NPPh ₂) ₂ Mo(CO) ₄	2024 m 1925 s 1908 s 1885 (sh)	957 (965) ^c	666 (465) ^e	Loses 2 × 2 CO LMo(CO) ₅ (1, 2 × 2)
<i>Trans</i> -(Me ₂ NPPh ₂) ₂ Mo(CO) ₄	1950 w 1897 s	955	666	Loses 1 × 4 CO
(Et ₂ NPPh ₂)Mo(CO) ₅	2073 w 1987 w 1947 s	920 (928)	493	Loses 1 × 5 CO
<i>Cis</i> -(Et ₂ NPPh ₂) ₂ Mo(CO) ₄	2024 s 1922 s 1911 s 1889 s	926	722	Loses 1 × 4 CO
<i>Trans</i> -(Et ₂ NPPh ₂) ₂ Mo(CO) ₄	1952 w 1895 s	924	722 (493) ^e	Loses 1 × 4 CO LMo(CO) ₅ (1 × 5)
(Pr ₂ NPPh ₂)Mo(CO) ₅	2073 w 1986 w 1946 s	1000 (990)	521	Loses 1, 2 × 2 CO
<i>Cis</i> -(Pr ₂ NPPh ₂) ₂ Mo(CO) ₄	2024 ms 1926 ms 1905 s 1897 s	985	521	LMo(CO) ₅ (1 × 5 CO)
<i>Trans</i> -(Pr ₂ NPPh ₂) ₂ Mo(CO) ₄	1952 w 1905 s	995	778 (521) ^e	Loses 1 × 4 CO LMo(CO) ₅ (1 × 5)
(Bu ₂ NPPh ₂)Mo(CO) ₅	2073 w 1988 w 1947 s	930 (928)	549	Loses 1, 2 × 2 CO
<i>Cis</i> -(Bu ₂ NPPh ₂) ₂ Mo(CO) ₄	2025 m 1927 s 1904 s 1880 (sh)	927	549	LMo(CO) ₅ (1 × 5 CO)
<i>Trans</i> -(Bu ₂ NPPh ₂) ₂ Mo(CO) ₄	1958 m 1901 s	930	549	LMo(CO) ₅ (1 × 5 CO)

^a KBr disc (Grubb Parsons Spectromaster). ^b $\nu(CO)$ (hydrocarbon)¹⁵: (Ph₃P)Mo(CO)₅ 2073, 1984 w, 1952 cm^{-1} ; *cis*-(Ph₃P)₂Mo(CO)₄ 2022, 1929, 1911, 1899 cm^{-1} ; *trans*-(Ph₃P)₂Mo(CO)₄ 1952 vw, 1903 cm^{-1} .

^c $\nu(P-N)$ free ligand. ^d ⁹⁶Mo isotope (AEI MS-9 spectrometer). ^e LMo(CO)₅ parent ion.

toluene at 80° (2–5 h) gave good yields of $(R_2NPPh_2)Mo(CO)_5$ as air-stable crystalline solids. Analogous reactions using R_2NPPh_2 (R = Me, Et) gave only starting materials. However (Et₂NPPh₂)Mo(CO)₅ was prepared via a Carius tube reaction at 150° in toluene. We were unable to prepare (Me₂NPPh₂)Mo(CO)₅ under a variety of experimental conditions.

Reaction between (bicyclo[2.2.1]hepta-2,5-diene)Mo(CO)₄ and R_2NPPh_2 in 1/2 molar amounts in toluene at 25° gave *cis*-(R_2NPPh_2)₂Mo(CO)₄ in all cases. Analogous reactions at 80° yielded the *trans* isomer, except for Bu₂NPPh₂ which gave

a *cis/trans* mixture.

Products were isolated by vacuum removal of solvent and trituration with nitromethane. Compounds were recrystallised either from toluene/hexane or hexane/nitromethane mixtures. Physical properties and analytical data for the complexes are given in Table 1, NMR data in Table 2, IR and mass spectral data in Table 3. Heating R_2NPPh_2 ($R = Et, Pr$) and $Mo(CO)_6$ in equimolar amounts in toluene for 16 h/250° under autogenous pressure, gave a red complex in both cases which contained no nitrogen and corresponded to the symmetrical phosphorus-bridged dinuclear complex $[Mo(CO)_4PPh_2]_2$ ¹.

DISCUSSION

Since the carbonyl IR frequencies in metal carbonyls are sensitive to π -bonding in other attached ligands, one might expect any appreciable N-P interaction in R_2NPPh_2 , due to $p_\pi-d_\pi$ electron delocalisation, to be reflected in a reduction of the carbonyl frequency in $(R_2NPPh_2)_xMo(CO)_y$, in comparison with the corresponding $(Ph_3P)_xMo(CO)_y$ derivatives¹⁵. However Table 3 shows that no significant differences occur, and hence the ability of phosphorus to accept electrons from the metal, as measured by $\nu(C\equiv O)$ changes, is not affected by bonding to nitrogen. Similar conclusions were reached from a study of $[(Ph_2P)_2NR]Mo(CO)_4$ ¹¹. The complexes prepared with Me_2NPPh_2 as ligand exhibit the characteristic absorption of the $>N-Me$ group at $\sim 2800\text{ cm}^{-1}$ which indicates that phosphorus is the donor atom, since this absorption disappears on N-coordination¹³.

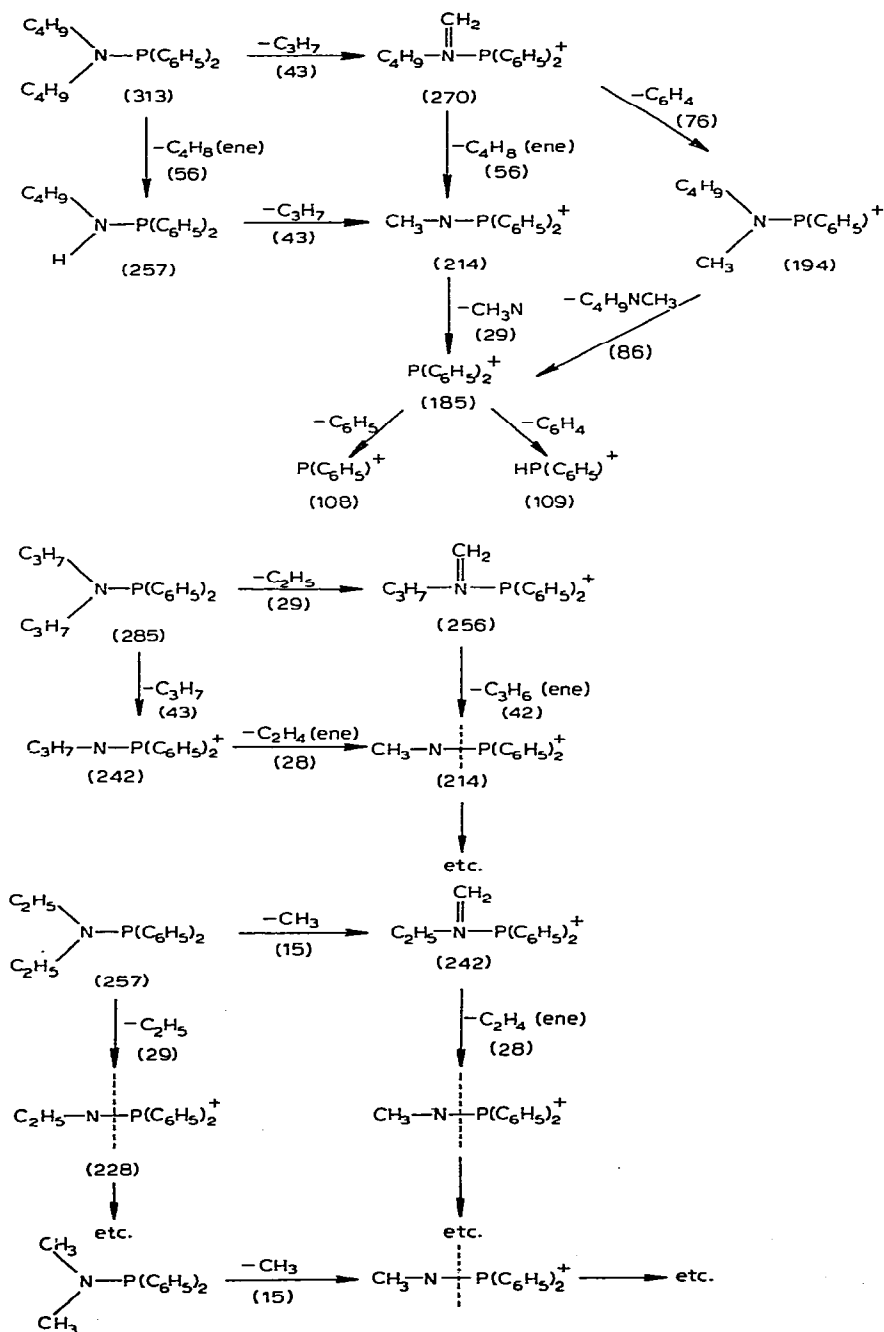
Dipole moment (Table 1)-and NMR data (Table 2) of the complexes are in accord with the assigned structures and do not warrant further comment.

Molecular weight data (ebullioscopic in benzene) for $(R_2NPPh_2)_2Mo(CO)_5$ agree well with the calculated values (± 20). However the values obtained for *cis*- and *trans*- $(R_2NPPh_2)_2Mo(CO)_4$ indicate extensive dissociation.

Mass spectral results (Table 3) are complicated by thermal decomposition of $(R_2NPPh_2)_2Mo(CO)_4$ due to the relatively high inlet temperature (180–200°). Parent ions were satisfactorily obtained for $(R_2NPPh_2)Mo(CO)_5$ ($R = Et, Pr, Bu$) with subsequent loss of carbonyl groups. Although $(Et_2NPPh_2)Mo(CO)_5$ loses five CO groups in stepwise fashion, the analogous complexes where $R = Pr, Bu$, after loss of the first CO, lose the remaining ones in pairs. Similar results have been observed with $(C_5H_5)(L)V(CO)_3$, $L_2Fe(CO)_3$ [$L = (Me_2N)_3P$]⁷ and $[(C_6H_5)Fe(CO)_2]_2$ ¹⁶. For *cis*- $(Me_2NPPh_2)_2Mo(CO)_4$ the parent ion is observed, in addition to ions arising from $(Me_2NPPh_2)Mo(CO)_5$ with prevalent loss of CO groups in pairs occurring in both cases. King⁷ observed that *trans*- $[(Me_2N)_3P]_2Mo(CO)_4$ gives rise to $[(Me_2N)_3P]Mo(CO)_5$ under similar conditions. In the case of *cis*- $(R_2NPPh_2)_2Mo(CO)_4$ ($R = Pr, Bu$) the only parent ion observed is $(R_2NPPh_2)Mo(CO)_5$ with stepwise loss of CO groups. No evidence of $(R_2NPPh_2)_3Mo(CO)_3$ was found which might be expected if disproportionation occurred *i.e.* $2 L_2Mo(CO)_4 \rightarrow LMo(CO)_5 + L_3Mo(CO)_3$. Parent ions were observed for *trans*- $(R_2NPPh_2)_2Mo(CO)_4$ ($R = Me, Et, Pr$) but again $(R_2NPPh_2)Mo(CO)_5$ was also present, ($R = Et, Pr$). For *trans*- $(Bu_2NPPh_2)_2Mo(CO)_4$ only $LMo(CO)_5$ was observed as parent ion.

Following loss of carbonyl groups from the above complexes, the ions $(R_2NPPh_2)_xMo^+$ break down further by loss of metal and subsequent decomposition of

SCHEME 1



the ligand. The cracking patterns of the free ligands suggest the elimination reactions shown in Scheme 1.

It is of interest to compare the $\text{CH}_2\text{N(R)PPh}_2$ fragments observed in this work with the elimination of CH_2NMe from $(\text{Me}_2\text{N})_3\text{P}$ derivatives of metal carbonyls reported by King⁷ and Braterman⁸. However, whereas these workers suggest metal species of type $\text{R}_2\text{NP}(\text{CH}_2\text{NCH}_2)\text{Mo}^+$ containing M–C bonds and also fragments with M–N bonds *e.g.* $(\text{Me}_2\text{N})_3\text{P–M–NMe}_2^+$, this behaviour has not been observed with R_2NPPh_2 .

The high temperatures needed to cleave the P–N bond in these molybdenum derivatives also facilitates the loss of organic groups attached to nitrogen (cracking pattern) and therefore precludes the isolation of products containing both $\text{R}_2\text{N-}$ and $\text{Ph}_2\text{P-}$ bridging groups. This would explain the formation of the diphosphido-bridged species $(\text{OC})_4\text{Mo}(\text{Ph}_2\text{P})_2\text{Mo}(\text{CO})_4$ under such conditions. The only other reported attempt to prepare binuclear phosphorus- and nitrogen-bridged species is that of Grobe¹⁷ who reacted manganese carbonyl with perfluoromethylphosphorus derivatives including $(\text{CF}_3)_2\text{PNMe}_2$. However, cleavage of the P–N bond occurred and a diphosphido-bridged product resulted.

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