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MOLYBDENUM CARBONYL COMPLEXES OF UNSATURATED TERTIARY PHOSPHINES

PHILIP E. GARROU and GEORGE E. HARTWELL

*Department of Chemistry**, *Indiana University, Bloomington, Indiana* 47401 (*U.S.A.*)

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SUMMARY

The photochemical and thermal reactions between $Mo(CO)_6$, $Mo(CO)_4$-norbornadiene, $Mo(CO)_3$-cycloheptatriene or $Mo(CO)_4Cl_2$ and the ligands $Ph_nP(CH_2CH_2CH{=}CH_2)_{3-n}$, where $n=0,1$ or 2, yield a variety of complexes in which the olefin has an influence on the products that can be isolated. Although chelated products are formed, the maximum coordinating ability of each ligand is not realized during olefin replacement reactions. Species are formed that contain an increased number of carbonyls or that polymerize in preference to chelation through metal–olefin bond formation. These species are not analogous to the products obtained with saturated tertiary phosphines.

INTRODUCTION

A comparison of the substitution reactions of chlorotris(2-vinylphenyl)-phosphinorhodium(I)[1] Rh(CO)Cl(Tvp), chlorotris(2-vinylphenyl)arsinorhodium(I)[1] Rh(CO)Cl(Tva), and chlorotri-3-butenylphosphinorhodium(I)[2] Rh(CO)Cl(Tbp), indicates that although the three complexes are structurally similar with tetradentate phosphine–olefin ligands, the latter two undergo facile substitution of a metal–olefin bond by bases such as CO or Ph_3P, while the aryl phosphine complex is much less reactive. The difference in reactivity can be attributed to both the donor–acceptor ability of the Group V atom and the steric requirements of each ligand.

A related bidentate ligand, 2-vinylphenyldiphenylphosphine (Mvp) reacts with molybdenum tetracarbonyl norbornadiene, $Mo(CO)_4$Nbd, to give 50–70% yields of $Mo(CO)_4$Mvp[3]. Two other aryl phosphine–olefin ligands, 2-allylphenyldiphenylphosphine and *cis*-2-propenylphenyldiphenylphosphine undergo the same reaction to yield complexes of the type $Mo(CO)_4L$[4]. $Mo(CO)_4$Mvp can also be prepared, in 20–30% yields, in a direct reaction with $Mo(CO)_6$, however complexes containing more than one ligand per molybdenum could not be isolated from any of the reaction mixtures[3]. The difference in the chemical behavior of the rhodium complexes containing tri-3-butenylphosphine (Tbp), instead of tris(2-vinylphenyl)phosphine (Tvp), prompted us to synthesize the molybdenum tetracarbonyl derivative of the potentially bidentate 3-butenyldiphenylphosphine (Mbp).

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* Contribution no. 2183.

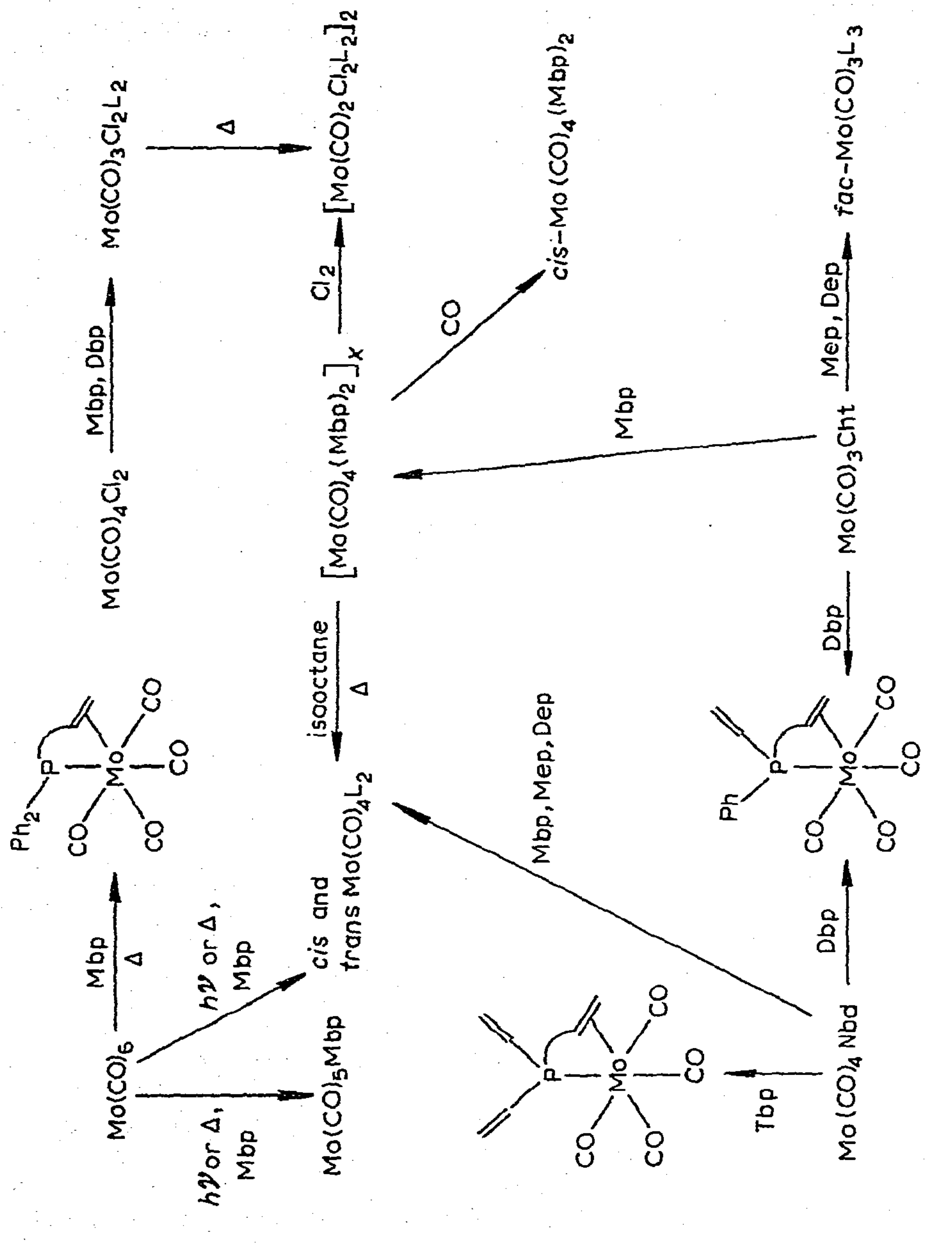


Fig. 1. The preparation of molybdenum phosphine complexes.

Although Mbp is structurally similar to Mvp, the reaction with $Mo(CO)_4Nbd$ does not yield $Mo(CO)_4Mbp$, but gives instead a mixture of *cis* and *trans* $Mo(CO)_4(Mbp)_2$. This unexpected result further prompted a series of thermal and photochemical reactions involving Mbp, Dbp(di-3-butenylphenylphosphine) and Tbp with $Mo(CO)_6$, $Mo(CO)_4Nbd$ and molybdenum tricarbonyl cycloheptatriene, $Mo(CO)_3Cht$.

The mechanisms for substitution involving displacement of unsaturated hydrocarbon ligands have not been well defined[5]. Werner[6] proposed that $Mo(CO)_4$-Nbd reacts by an S_N1 mechanism involving partial cleavage of the metal–diene bond, followed by either recombination or displacement by another ligand. For $Mo(CO)_3$-Cht, substitution is thought to be by an S_N2 mechanism. Reactions with monodentate ligands usually leads to *facial*-tris-substituted products[7]. Kinetic studies are consistent with S_N2 reaction mechanism[8,9].

Harrill and Kaesz[10] reported that reaction of $Mo(CO)_4Nbd$ with ^{13}CO was not stereospecific and that the rate of CO scrambling was of the same order as ligand substitution and thus both *cis*- and *trans*-$Mo(CO)_4(L)_2$ could be expected with monodentate ligands.

In order to determine whether or not the olefin influences the course of substitution reactions on molybdenum carbonyls (Fig. 1), and for comparison of infrared spectra in assigning structures to products, the ligands, ethyldiphenylphosphine, Mep, and diethylphenylphosphine, Dep, whose donor–acceptor abilities should be similar to Mbp and Dbp respectively, were treated under similar conditions. The substitution products of these saturated ligands are typical of those reported for tertiary phosphines and have similar IR spectra[11].

RESULTS AND DISCUSSION

Reactions with molybdenum tetracarbonyl norbornadiene, $Mo(CO)_4Nbd$

Reaction of $Mo(CO)_4Nbd$ with Mbp at various metal to ligand ratios, does not give a complex in which the ligand is bidentate as previously reported for the aryl phosphine–olefin ligands, but yields *cis* and *trans* disubstituted complexes as observed with the saturated ligands, Mep and Dep. Changes in reaction time, temperature and solvent fail to produce any chelated products.

In contrast, the reaction of $Mo(CO)_4Nbd$ with Dbp yields $Mo(CO)_4Dbp$ in which the potentially tridentate ligand is coordinated through phosphorous and a single olefin. The second olefin, however, does not displace an additional carbonyl.

The coordinated olefin can be detected in the infrared by the presence of an absorption at 1535 cm^{-1}. The shift of this absorption from that of the free olefin, 1637 cm^{-1}, is smaller than that observed for $Mo(CO)_4Mvp^3$ (102 cm^{-1} *vs.* 120 cm^{-1}) and may be an indication of a weaker metal–olefin interaction in $Mo(CO)_4Dbp$.

The PMR spectrum (Fig. 2) shows the three protons of the bonded olefin shifted upfield, with a corresponding reduction in the coupling constants among these protons, indicative of the metal–olefin interaction. The PMR spectrum is further complicated by the presence of equal quantities of the two isomeric forms that are a consequence of the asymmetric poshoprus. The ^{31}P magnetic resonance spectrum is consistent with this assignment and has two peaks of equal intensity separated by 1.8 ppm. Although solutions of $Mo(CO)_4Dbp$ are air-sensitive, thus precluding accurate

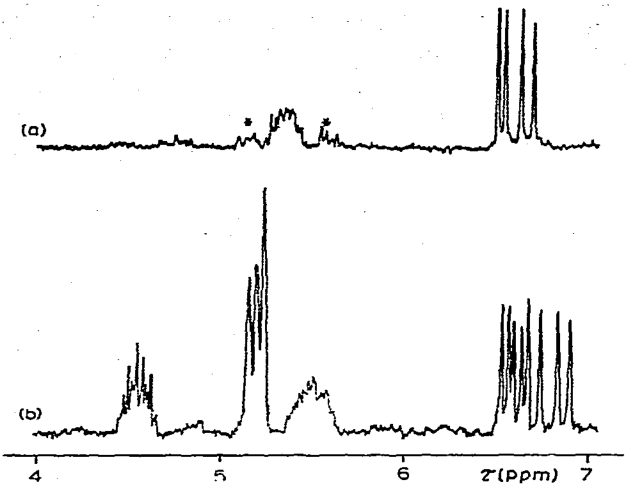


Fig. 2. 220 MHz PMR spectra of (a) $Mo(CO)_4Mbp$ and (b) $Mo(CO)_4Dbp$; *impurity of $Mo(CO)_4(Mbp)_2$

molecular weight determinations, the possibility of a dimeric formulation with bridging phosphine–olefin ligands, can be excluded, since such species would have several isomeric configurations and the ^{31}P and ^{1}H NMR spectra would be further complicated.

The two sets of bonded olefinic peaks indicate that there is no exchange between the bonded and non-bonded olefins on the complex on the NMR time scale, and that the metal–olefin bond is not isomerizing through bond breaking and reassociation of the same olefin. Molecular models show that the olefin can undergo a restricted rotation of about 90°, from a configuration with the olefin perpendicular, to one with the olefin parallel to the molybdenum–phosphorus bond (Fig. 3) but further rotation, (leading to isomerization) is not possible without bond breakage. There are actually four isomers of $Mo(CO)_4Dbp$ present in solution, two related by the interchange of the phenyl and non-bonded butene, and their optical isomers.

In a similar manner, Tbp reacts with $Mo(CO)_4Nbd$ to yield $Mo(CO)_4Tbp$ in which this potentially tetradentate ligand is only bidentate, with two non-bonded olefinic groups. The NMR spectrum of this complex shows only one type of bonded olefin (the phosphorus is not asymmetric) and the complex is undoubtedly monomeric.

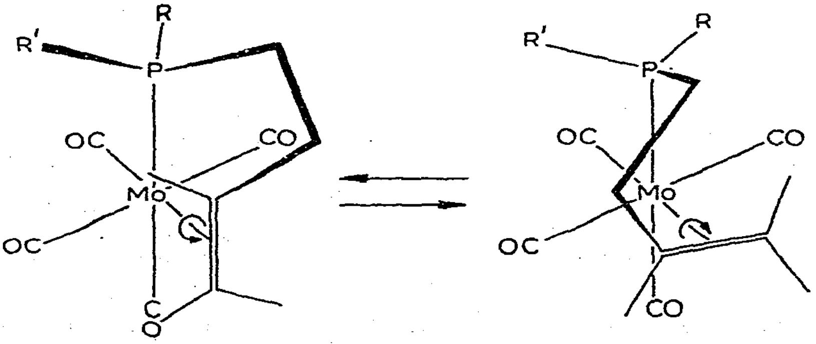


Fig. 3. Restricted olefin rotation for one isomer of $Mo(CO)_4L$.

It appears that, as with the rhodium complexes, the aryl phosphine–olefin ligands are more likely to chelate than the corresponding alkyl ligands. However, in treating Dpb or Tbp instead of Mbp, the concentration of olefin is effectively increased at each molybdenum and as a result the probability of chelation increases over that of the coordination of a second phosphine. In none of the reactions involving displacement of Nbd has any of the three ligands attained its maximum coordination.

Reactions with molybdenum tricarbonyl cycloheptatriene, $Mo(CO)_3Cht$

Since Mbp reacted with $Mo(CO)_4Nbd$ in a manner analogous with the saturated phosphines, Mep and Dep, it was expected that reaction of Mbp with $Mo(CO)_3$-Cht would produce the tri-substituted product *fac*-$Mo(CO)_3(Mbp)_3$, although there is the possibility of one bidentate ligand and the complex $Mo(CO)_3(Mbp)_2$. The yellow powder resulting from the reaction has repeated C–H analyses consistent with $[Mo(CO)_4(Mbp)_2]_x$. The PMR, IR and Raman spectra are decidedly different from either the *cis* or *trans* isomers of the same formulation, and there is no indication of metal–olefin bonding in any of the spectra. Although the IR bands are at 1940 cm^{-1} and lower, consistent with a complex in which there are no mutually *trans* carbonyl groups, the symmetry of the complexes $Mo(CO)_3(Mbp)_2$ and $Mo(CO)_3(Mbp)_3$ also require the IR and Raman spectra to be coincidental, and this was not observed. The absence of bridging carbonyls absorptions in the IR leads to the conclusion that the complex is polymeric with Mo–Mo bonds and contains seven coordinate molybdenum.

The complex can be isomerized to a mixture of *cis* and *trans* $Mo(CO)_4(Mbp)_2$ by refluxing in isooctane, and the single isomer, *cis*-$Mo(CO)_4(Mbp)_2$, can be prepared by bubbling carbon monoxide through a toluene solution of the polymeric complex. The reaction of the complex with chlorine in cyclohexane gives $[Mo(CO)_2Cl_2(Mbp)_2]_2$.

Reaction of $Mo(CO)_3Cht$ with Dbp did not yield the complex with a tridentate ligand, but gave the same two isomers of $Mo(CO)_4(Dbp)_2$ obtained from $Mo(CO)_4$-Nbd. No product could be isolated from the reaction with Tbp.

Thus, in both of the $Mo(CO)_3Cht$ reactions, the products obtained do not utilize the maximum coordination of the ligands, nor are they the result of simple tris-*fac* substitution. In contrast to the reactions of the saturated ligands Mep and Dep with $Mo(CO)_3Cht$, a carbonyl is added to the molybdenum in each case. The addition of carbon monoxide, supplied by decomposition of a second molecule in solution, has been reported for reactions involving the ligands tris(dimethylamino)phosphine and tris(dimethylamino)arsine[12], but was not expected in our reactions since the coordination number of the metal could be satisfied by an olefin. It is also surprising that the polymeric complex $[Mo(CO)_4(Mbp)_2]_x$ forms in preference to the simpler hexacoordinate isomers of a complex in which one ligand is bidentate. It is possible that the olefin governs the formation of the polymer by initially coordinating to two different metal atoms in an intermediate complex.

The addition of a carbon monoxide to the molybdenum species can occur by two mechanisms. The first, suggested by King[12], is an outer sphere mechanism in which a carbon monoxide is lost to solution through thermal dissociation of a complex and then reacts with a second complex before it can leave the solution.

A second mechanism, which would be more efficient, involves transfer from one metal to another by a bridging carbonyl intermediate.

In two separate reactions involving Dbp, using the described reaction conditions, yellow compounds that are very air sensitive were obtained instead of the usual products.

$$Mo(CO)_4Nbd + Dbp \rightarrow \nu(CO),\ 1895s,\ 1757s,\ 1748s$$

$$Mo(CO)_3Cht + Dbp \rightarrow \nu(CO),\ 1945s,\ 1894s,\ 1853s,\ 1814s,\ 1750s$$

The presence of bridging carbonyls in these complexes supports the possibility of carbonyl transfer involving polymeric intermediates, and it is possible such intermediates are present even in the more typical substitution reactions involving molybdenum carbonyls.

The isolation of these two species containing carbonyl bridges may be a consequence of the phosphine-olefin ligand which can act as a chelate and thus preserve a coordination site until reaction with a second molecule takes place. The chelate may then give way to carbonyl bridge formation with loss of the weak metal–olefin interaction. The infrared spectra of these carbonyl bridged complexes show no sign of metal–olefin bonding in the solid state. The complexes decompose in solution thus precluding PMR studies.

Thermal and photochemical reactions with $Mo(CO)_6$

Nyholm *et al.*, obtained $Mo(CO)_4Mvp$ in 20–30% yields by a thermal reaction in methylcyclohexane or toluene. The reaction in toluene is faster with somewhat better yields[3]. The reaction of Mbp with $Mo(CO)_6$ in isooctane for two days at reflux gave no evidence, by IR or PMR, of a chelated complex whereas after 36 h in toluene a 1–4% yield of $Mo(CO)_4Mbp$ can be observed along with $Mo(CO)_5Mbp$, *cis*- and *trans*-$Mo(CO)_4(Mpb)_2$ and unreacted $Mo(CO)_6$. Further reflux does not convert $Mo(CO)_5Mbp$ into $Mo(CO)_4Mbp$ and after 60 h the mixture of the five complexes is unchanged, *cis*- and *trans*-$Mo(CO)_4(Mbp)_2$ are the major substituted products.

$Mo(CO)_4Mbp$ can be identified by its IR spectrum $\nu(C{=}C)$, 1535 cm^{-1}, and the upfield shift and reduced coupling of the olefinic protons, similar to those already noted for $Mo(CO)_4Dbp$ (Fig. 2). An analytically pure sample was not obtained due to the small yields and the difficulty in separation from *cis*-$Mo(CO)_4(Mbp)_2$.

The irradiation of $Mo(CO)_6$ and Mbp in cyclohexane yielded some $Mo(CO)_5$-Mbp along with *cis*- and *trans*-$Mo(CO)_4(Mbp)_2$, however no $Mo(CO)_4Mbp$ was detected. As with the thermal reaction, further reaction does not convert $Mo(CO)_5$-Mbp into $Mo(CO)_4Mbp$.

The preparation of molybdenum(II) Complexes with Mbp and Dbp

Colton has prepared the seven coordinate yellow complex $Mo(CO)_3Cl_2(PPh_3)_2$ by the reaction of $Mo(CO)_4Cl_2$ with PPh_3. Subsequent heating in solution gives the blue monomeric six coordinate $Mo(CO)_2Cl_2(PPh_3)_2$[13–15]. The reaction of Mbp or Dbp with $Mo(CO)_4Cl_2$ gives the seven coordinate complexes $Mo(CO)_3Cl_2L_2$ in the same manner as with PPh_3. Heating these complexes in CH_2Cl_2 however, does not give blue compounds but yellow complexes $[Mo(CO)_2Cl_2L_2]_2$ analogous to the reported complex $[Mo(CO)_2Cl_2(PMe_2Ph)_2]_2$, which has been assigned a dimeric structure on the bases of the $\nu(Mo{-}Cl)$ at 299, 290, 234 and 228 cm^{-1}[16]. The complex $[Mo(CO)_2Cl_2(Mbp)_2]_2$ has corresponding bands at 281, 278 and 235 cm^{-1}. The dimer is paramagnetic, μ 2.33 BM (Faraday method) and was also prepared from the chlorination of $[Mo(CO)_4(Mbp)_2]_x$.

Dimerization is therefore favored over replacement of the CO by an olefin in the seven coordinate species, even though PPh_3 is able to prevent such a dimerization, presumably a result of steric hindrance.

EXPERIMENTAL

Infrared spectra were recorded on Perkin–Elmer 137-G and 621 spectrometers. Raman spectra were obtained on a Cary 81 spectrometer using the He–Ne laser excitation at 6328Å. Proton magnetic resonance spectra were obtained on Varian HA 100 and Varian HR 220 spectrometers. The ^{31}P magnetic resonance spectra were obtained at 24.3 MHz on a modified Varian DP60 using Fourier Transform pulse methods. Irridiations were carried out using a water cooled 550W, Hanovia high pressure mercury vapor lamp. Analyses were carried out by Galbraith Industries, Knoxville, Tennessee.

All reactions were run under an argon atmosphere and all solvents were dried over sodium and deaerated immediately prior to use. Compounds were found to be air stable except in solution. They were recrystallized from isooctane.

The starting materials $Mo(CO)_4Nbd$[17], $Mo(CO)_3Cht$[7], $Mo(CO)_4Cl_2$[13] and the ligands[18] Mbp, Dbp and Tbp were prepared by literature methods.

Reaction of Mo(CO)₄Nbd with Mbp

Reaction of the monobutene ligand in refluxing toluene or isooctane gives *cis*- and *trans*-$Mo(CO)_4(Mbp)_2$, the ratio of *cis* to *trans* was found to decrease with time. In a typical reaction, 0.30g of $Mo(CO)_4$ Nbd is refluxed in 50 ml toluene with 0.24 ml of ligand. After 15 h, removal of solvent gives a 1/4 mixture of *cis* and *trans* isomers (by ^{31}P NMR). The *trans* isomer can be separated by fractional crystallization from isooctane. Yield ca. 40%, m.p. *cis* 154–156°, m.p. *trans* 159–161°. (Found: C, 62.42; H, 4.98. $C_{36}H_{34}MoO_4P_2$ calcd.: C, 62.71; H, 4.96%.)

Reaction of Mo(CO)₄Nbd with Dbp

Reaction with the dibutene ligand over varying periods of time produces equal quantities of the two isomeric forms of $Mo(CO)_4Dbp$. In a typical reaction, 0.60g of $Mo(CO)_4Nbd$ and 0.44 ml of Dbp were refluxed in toluene or isooctane for 6 h. The product was isolated by subsequent removal of solvent. Yield ~50%, m.p. 114–115°. (Found: C, 50.09; H, 4.59. $C_{18}H_{19}MoO_4P$ calcd.: C, 50.71; H, 4.52%.)

Reaction of Mo(CO)₄Nbd with Tbp

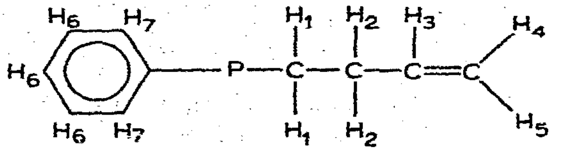
Several reactions of the tri-butene ligand in toluene or isooctane were attempted using temperatures from $-10°$ to $+97°$, and times from 1 h to 15 h gave only low yields. (ca. 5%) of $Mo(CO)_4Tbp$.

Reaction of Mo(CO)₃Cht with Mbp

Reaction of the monobutene ligand in isooctane, resulted in the preparation of $[Mo(CO)_4(Mbp)_2]_x$. In a typical reaction 1.0 ml of Mbp is added to 0.50 g of $Mo(CO)_3Cht$ in 50 ml of isooctane at room temperature and a yellow powder immediately begins to precipitate. A change of solvent to toluene, yielded the same product. Yields ~75%, m.p. 111–113°. (Found: C, 62.71; H, 4.83. $C_{36}H_{34}MoO_4P_2$ calcd.: C, 62.71; H, 4.96%.)

TABLE 1

^1H AND ^{31}P NMR DATA[a]



Compound	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7	δP^b	$J_{34}(Hz)$	$J_{35}($
Mbp, $Ph_2PC_4H_7$		7.9^c	4.19	5.11	5.06	2.70	2.60	+17.0	10.0	17.0
Dbp, $PhP(C_4H_7)_2$	8.20	7.92	4.17	5.08	5.00	2.68	2.52	+25.4	10.0	17.0
Tbp, $P(C_4H_7)_3$	8.51	7.83	4.15	5.04	4.97				10.20	17.1
$Mo(CO)_4Mbp$		8.14^c	5.34^d	6.53^d	6.67^d	3.05	2.60		8.5^d	14.3^d
$Mo(CO)_4Dbp$		8.2^c	4.55		5.17^c	2.89	2.60	−42.5, −44.3		
			5.5^d	6.62^d	6.86^d				9.0^d	15.0^d
			5.4^d	6.55^d	6.71^d				9.0^d	15.0^d
$Mo(CO)_4Tbp$		8.3^c	4.34		5.00^c					
			5.35^d	6.47^d	6.70^d				9.0^d	14.0^d
$Mo(CO)_4(Mbp)_2$	7.43	7.77	4.37	5.39	5.12	2.96	2.45	−25.8 *cis* −38.5 *trans*	9.9	17.0
$[Mo(CO)_4(Mbp)_2]_x$		7.9^c	4.48		5.22^c	3.02	2.68			
$Mo(CO)_3Cl_2(Dbp)_2$		7.6^c	4.37	5.13	5.05	3.02	2.47	+12.2	9.9	17.0

[a] Ligands in $CDCl_3$, complexes in C_6D_6, for PMR: the first five compounds at 220 MHz, the remaining four at 100 M

[b] In ppm *vs.* 85% H_3PO_4. [c] Center of unresolved peaks. [d] Bonded olefin.

Reaction of $[Mo(CO)_4(Mbp)_2]_x$ *with CO*

CO was bubbled through a toluene solution of $[Mo(CO)_4(Mbp)_2]_x$ for 2 h, the reaction followed by infrared spectroscopy. The solvent was removed and the resulting oil crystallized from isooctane to yield *cis*-$Mo(CO)_4(Mbp)_2$ and no sign of the *trans* isomer. m.p. 154–156°.

Reaction of $[Mo(CO)_4(Mbp)_2]_x$ *in refluxing solvent*

From a solution of $[Mo(CO)_4(Mbp)_2]_x$, in toluene which had refluxed for 15 h, 50% of the starting material was obtained unchanged along with decomposition product. Refluxing for 15 h in isooctane produced a mixture of *cis*- and *trans*-$Mo(CO)_4(Mbp)_2$ as characterized by its IR.

Reaction of $[Mo(CO)_4(Mbp)_2]_x$ *with* Cl_2

0.01 g of $[Mo(CO)_4(Mbp)_2]_x$ was added to 50 ml of cyclohexane which had been previously saturated with Cl_2. The solution quickly became orange and a tannish solid precipitated which did not have a carbonyl absorption in the IR. Solvent was removed from the orange solution and subsequent recrystallization from hexane gave a 40% yield of $Mo(CO)_2Cl_2(Mbp)_2$, m.p. 115°. Analysis and IR agree with product derived from $Mo(CO)_4Cl_2$.

Reaction of $Mo(CO)_3Cht$ *with Dbp*

Reaction of 0.6 g $Mo(CO)_3Cht$ with 0.3 ml of Dbp in isooctane for a period of 3 h and subsequent removal of solvent gave a 40% combined yield of the two iso-

TABLE 2

	ν(C=O) *infrared and (Raman)*[a] *(cm^{-1})*						*Other infrared absorptions*[a] *(cm^{-1})*
$\text{Mo(CO)}_5\text{Mbp}$	2075 m		1955	1946			
$\text{Mo(CO)}_5\text{PPh}_3$[11]	2073	1984 w	1952				
$\text{Mo(CO)}_4\text{Mbp}$		2022	1938	1889	1886		ν(C=C), 1535 w
$\text{Mo(CO)}_4\text{Dbp}$		2026	1930	1912	1860		ν(C=C), 1535 w
		(2023	1929	1915 (sh)	1857)		
$\text{Mo(CO)}_4\text{Tbp}$		2016	1925	1903	1860		ν(C=C), 1538 w
$\text{Mo(CO)}_4\text{Mvp}$[3]		2035	1950	1910	1885		ν(C=C), 1505 w
cis-$\text{Mo(CO)}_4\text{(Mbp)}_2$		2020	1925	1903	1894		
cis-$\text{Mo(CO)}_4\text{(PPh}_3)_2$[11]		2022	1929	1911	1899		
trans-$\text{Mo(CO)}_4\text{(Mbp)}_2$		(2019	1942)		1890		
trans-$\text{Mo(CO)}_4\text{(PPh}_3)_2$[11]			1952 vw		1903		
$[\text{Mo(CO)}_4\text{(Mbp)}_2]_x$			1940	1844	1819		
				(1868	1824)		
fac-$\text{Mo(CO)}_3\text{(PPh}_3)_3$[11]			1934		1835		
$\text{Mo(CO)}_3\text{Cl}_2\text{(Mbp)}_2$		2010	1945	1911			
$\text{Mo(CO)}_3\text{Cl}_2\text{(Dbp)}_2$		2010	1945	1911			
$\text{Mo(CO)}_3\text{Cl}_2\text{(PPh}_3)_2$[13]		2045 m	1952	1903 m			
$[\text{Mo(CO)}_2\text{Cl}_2\text{(Mbp)}_2]_2$			1943 br		1845 br		ν(Mo–Cl), 281, 278 (sh), 235
$[\text{Mo(CO)}_2\text{Cl}_2\text{(Dbp)}_2]_2$			1940 br		1845 br		
$[\text{Mo(CO)}_2\text{Cl}_2\text{(PPhMe}_2)_2]_2$[16]		2024 vw	1942 (sh)	1921 vs	1850 vs	1815 (sh)	ν(Mo–Cl), 299, 290, 234 (sh), 228
$\text{Mo(CO)}_2\text{Cl}_2\text{(PPh}_3)_2$[14]			1960		1890		

[a] Absorptions are strong unless otherwise stated br = broad, sh = shoulder; new compounds were run as nujol mulls.

mers of $\text{Mo(CO)}_4\text{Dbp}$. Analysis, IR, and m.p. agree with product derived from $\text{Mo(CO)}_4\text{Nbd}$.

Reaction of $\text{Mo(CO)}_3\text{Cht}$ with Tbp

Repeated reaction of the tri-butene ligand in both toluene and isooctane at varying temperatures and times gave no isolatible product.

Thermal reaction of Mo(CO)_6 with Mbp

Reaction of Mo(CO)_6 and Mbp in refluxing toluene over varying times (12–60 h) and concentrations (0.01–0.1 moles) resulted in the production of $\text{Mo(CO)}_5\text{Mbp}$, *cis* and *trans* $\text{Mo(CO)}_4\text{(Mbp)}_2$ and $\text{Mo(CO)}_4\text{Mbp}$ in varying amounts along with unreacted Mo(CO)_6. In a typical reaction, 0.25 g Mo(CO)_6 in 50 ml of refluxing toluene was treated with 0.2 ml of Mbp over a period of 36 h. The solvent was then reduced to ca. 1 ml, placed on an alumina column and eluted with hexane to remove $\text{Mo(CO)}_5\text{Mbp}$ and *trans*-$\text{Mo(CO)}_4\text{(Mbp)}_2$. Subsequent elution with 1/1 ether/benzene resulted in the isolation of *cis*-$\text{Mo(CO)}_4\text{(Mbp)}_2$ and $\text{Mo(CO)}_4\text{Mbp}$, the latter being obtained in 1–4% yields.

Photochemical reaction of Mo(CO)_6 with Mbp

UV irradiation of a cyclohexane solution of Mo(CO)_6 in the presence of Mbp resulted in approximately the same mixture of products as obtained in the thermal reaction. In a typical reaction 0.052 g $Mo(CO)_6$ and 0.048 g Mbp were irradiated in 50 ml of cyclohexane in a water cooled pyrex flask. After 2 minutes $Mo(CO)_5$Mbp appeared and longer reaction times produced in addition, *cis*- and *trans*-$Mo(CO)_4$-$(Mbp)_2$.

Reaction of $Mo(CO)_4Cl_2$ with Mbp or Dbp

The ligand, Mbp, 0.45 ml, was added to the $Mo(CO)_4Cl_2$ produced from 0.50 g of $Mo(CO)_6$ at −78°, as described by Colton[13]. The Dry Ice–acetone bath was removed and CO was allowed to evolve for 2 h. The solvent was then removed at room temperature and the oil thus obtained was crystallized at room temperature from isooctane to give a 45% yield of $Mo(CO)_3Cl_2(Mbp)_2$. Heating of the isooctane solution for a short time at ca. 60° resulted in the stoichiometric production of the yellow solid $[Mo(CO)_2Cl_2(Mbp)_2]_2$. (Found: C, 58.6; H, 4.84. $C_{34}H_{34}Cl_2MoO_2P_2$ calcd.: C, 58.1; H, 4.85%.)

In an analogous fashion, both products were obtained from Dbp (Found: C, 56.6; H, 5.7. $C_{30}H_{28}Cl_2MoO_2P_2$ calcd.: C, 56.2; H, 5.8%.)

CONCLUSIONS

The presence of the butene group on a tertiary phosphine alters the course of the reactions normally expected for photochemically and thermally induced reaction of phosphines with $Mo(CO)_6$ or its polyolefin derivatives.

In contrast to the aryl phosphine–olefin ligand, Mvp, the alkyl phosphine–olefin ligand, Mbp, does not chelate to form $Mo(CO)_4$Mbp as a major product, although it can be detected, in low yields, in the thermal reaction with $Mo(CO)_6$. The ligands, Dbp and Tbp, containing two or three butene groups do chelate, evidently a consequence of the increased probability for metal–olefin interaction. The successful chelation of Mvp thus appears to be primarily a result of its steric bulk and one less degree of freedom for rotation due to the presence of the aryl group.

The addition of an extra carbonyl during olefin replacement reactions (not observed with the saturated ligands, Mep and Dep) appears to be the result of a carbonyl transfer mechanism and in two instances species containing bridging carbonyls were isolated. The phosphine–olefin ligands may be instrumental in promoting the formation of such intermediates, but the carbonyl is preferred to a metal–olefin bond in the final product.

Even under irradiation, $Mo(CO)_5$Mbp does not lose a carbonyl to yield $Mo(CO)_4$Mbp.

Polymerization is also preferred to the metal–olefin bond, and the polymer $[Mo(CO)_4(Mbp)_2]_x$ can be isolated. For Mo^{II} the species $[Mo(CO)_2Cl_2(Mbp)_2]_2$ is formed in preference to a possible seven coordinate monomeric species with a metal–olefin bond replacing the carbonyl in $Mo(CO)_3Cl_2(Mbp)_2$.

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