Tetracarbonyl Diazaphosphole Complexes of Group 6B Metals: The Role of Steric Effects

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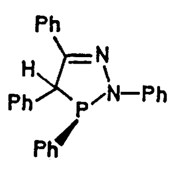
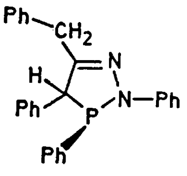
Thermal substitution reactions of $[M(CO)_5L^1{}_c]$ with *cis* diazaphosphole derivatives (L^1 = 3,4-dihydro-2,3,4,5-tetraphenyl-2*H*-1,2,3-diazaphosphole, $L^1{}_c$ and $L^1{}_t$ denote *cis* and *trans* L^1 respectively) have yielded a mixture of *cis* and *trans* (2 : 3 ratio) tetracarbonyl complexes in which the ligands are bonded through the phosphorus atom. In contrast the reactions of $[M(CO)_5L^1{}_t]$ with the bulkier *trans* diazaphosphole isomers ($L^1{}_t$ or $L^2{}_t$, L^2 = 5-benzyl-3,4-dihydro-2,3,4-triphenyl-2*H*-1,2,3-diazaphosphole) have only afforded the *trans* disubstituted tetracarbonyl $[M(CO)_4(L_t)_2]$. On the other hand, $L^1{}_t$ and $L^2{}_t$ have reacted with $[M(CO)_5L^1{}_c]$ affording the mixed-phosphine derivatives *trans*-$[M(CO)_4L^1{}_cL_t]$ ($L_t = L^1{}_t$ or $L^2{}_t$). The norbornadiene complex $[Mo(CO)_4(nbd)]$ produced only *cis*-$[Mo(CO)_4(L^1{}_c)_2]$ when treated with $L^1{}_c$ in cyclohexane at room temperature, whereas with $L^1{}_t$ no tetracarbonyl complexes (*cis* or *trans*) have been observed. In addition it has been found that *cis*(or *trans*)-$[Mo(CO)_4(L^1{}_c)_2]$ thermally interconverts by a dissociative pathway to the *trans*(or *cis*)-$[Mo(CO)_4(L^1{}_c)_2]$ to give an equilibrium composition (*cis* : *trans* = 2 : 3) whereas *trans*-$[Mo(CO)_4(L_t)_2]$ did not isomerize. All these different stereochemical results are tentatively explained by invoking fluxional or rigid five-co-ordinate intermediates in which only steric factors play a decisive role in determining the geometry and then the products distribution. The nature of the complexes has been established essentially by i.r. and ^1H n.m.r. spectra. An *X*-ray study on *cis*-$[Mo(CO)_4(L^1{}_c)_2]$ is also reported.

THE synthesis and separation of *cis* and *trans* disubstituted Group 6B tetracarbonyl complexes are generally not easy tasks.[1] Furthermore, the preparation of mixed-phosphine ligand complexes $[M(CO)_4LL']$ in both their isomeric forms presents a more complicated goal and so these complexes are vastly outnumbered by those with identical ligands.[2]

Recently we have investigated the complex forming properties of *cis*- and *trans*-3,4-dihydro-2,3,4,5-tetraphenyl-2*H*-1,2,3-diazaphosphole[3] ($L^1{}_c$ and $L^1{}_t$ respectively) with Group 6B metal carbonyls.[4] In this study it has been found that reaction of $[M(CO)_6]$ (M = Cr, Mo, or W) with $L^1{}_c$ or $L^1{}_t$ yielded the corresponding pentacarbonyl derivatives $[M(CO)_5L^1]$ in which the ligand is bonded through the phosphorus atom. However, on heating $[Mo(CO)_5L^1{}_c]$ in n-octane with additional $L^1{}_c$, a *cis–trans* mixture of disubstituted tetracarbonyls $[M(CO)_4(L^1{}_c)_2]$ was obtained. In contrast, under the same conditions $[Mo(CO)_5L^1{}_t]$ and $L^1{}_t$ afforded only *trans*-$[Mo(CO)_4(L^1{}_t)_2]$. The cause of this difference in stereochemical behaviour has been tentatively ascribed to steric factors which force the more crowded $L^1{}_t$ ligands to occupy only mutual *trans* positions in the molybdenum tetracarbonyl derivatives.



L^1



L^2

In order to ascertain if the above assignment is correct, we now report an extension of our initial work. Thus the separation and the ready characterization of the disubstituted tetracarbonyl $[M(CO)_4L_2]$ and the mixed-ligand complex $[M(CO)_4L^1L^2]$ together with the factors involved in these reactions are described. In addition, the observed interconversion of *cis* and *trans* tetracarbonyl complexes is explained by the intervention of a fluxional five-co-ordinate species arising through ligand (CO or L) dissociation from the six-co-ordinate derivatives.

An *X*-ray study on *cis*-$[Mo(CO)_4(L^1{}_c)_2]$ is also reported.

RESULTS

When Group 6B pentacarbonyl derivatives $[M(CO)_5L^1{}_c]$ were allowed to react with an equimolar amount of $L^1{}_c$ in refluxing iso-octane for *ca.* 12 h a *cis–trans* mixture of disubstituted tetracarbonyl complexes $[M(CO)_4(L^1{}_c)_2]$, in which the diazaphosphole ligands are bonded through the P atoms, was obtained. Chromatographic separation of the reaction mixtures produced the two isomers, with a *cis* : *trans* ratio of about 2 : 3, in a total yield of *ca.* 65% for Cr, 75% for Mo, and 60% for W.

Different results were obtained if $[M(CO)_5L_t]$ ($L_t = L^1{}_t$ or $L^2{}_t$) was treated with additional L_t in refluxing n-octane or iso-octane for longer reaction times.† In all the cases examined only the *trans* disubstituted $[M(CO)_4(L_t)_2]$ was recovered after silica-gel chromatography. Under the same experimental conditions $L^1{}_t$ and $L^2{}_t$ react with $[M(CO)_5L^1{}_c]$ affording the mixed phosphine derivative *trans*-$[M(CO)_4L^1{}_cL_t]$ as the predominant reaction product. Similar results have been obtained in the reaction of $L^1{}_c$ with $[M(CO)_5L^1{}_t]$ and in both cases small variable quantities of $[M(CO)_5L^1{}_t]$, $[M(CO)_5L^1{}_c]$, *trans*-$[M(CO)_4(L^1{}_c)_2]$, *cis*-$[M(CO)_4(L^1{}_c)_2]$, and *trans*-$[M(CO)_4(L^1{}_t)_2]$ are obtained as side-reaction products. Their nature has been established by t.l.c. analysis, i.r. spectra and/or, where possible, by comparison of their n.m.r. spectra with those of authentic samples obtained as described above or previously.[3]

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† Solvents with lower boiling point are preferred to reduce thermal decomposition of the products.

It is worthwhile to note that the mixed-diastereoisomeric ligand complexes *trans*-$[\mathrm{M(CO)_4L^1_cL^1_t}]$ are obtained in a pure form (Cr 30%, Mo 40%, W 35%) by careful chromatographic separation from a mixture containing a distribution of all the described complexes. Table 1 contains a summary of the thermal substitution reactions investigated in this study, along with the stereochemistry of the resulting products.

TABLE 1

Summary of the thermal substitution reactions on $[\mathrm{M(CO)_5L}]$ (M = Cr, Mo, or W)

Compound thermolized	Entering ligand	Stereochemistry of products
$[\mathrm{M(CO)_5L^1_c}]$	$\mathrm{L^1_c}$	*cis-trans*-$[\mathrm{M(CO)_4(L^1_c)_2}]$ (*ca.* 2 : 3)
$[\mathrm{M(CO)_5L^1_t}]$	$\mathrm{L^1_t}$	*trans*-$[\mathrm{M(CO)_4(L^1_t)_2}]$
$[\mathrm{M(CO)_5L^1_c}]$	$\mathrm{L^1_t}$	*trans*-$[\mathrm{M(CO)_4L^1_cL^1_t}]$
$[\mathrm{M(CO)_5L^1_t}]$	$\mathrm{L^1_c}$	*trans*-$[\mathrm{M(CO)_4L^1_cL^1_t}]$
$[\mathrm{Mo(CO)_5L^1_c}]$	$\mathrm{L^2_t}$	*trans*-$[\mathrm{M(CO)_4L^1_cL^2_t}]$
$[\mathrm{Mo(CO)_5L^2_t}]$	$\mathrm{L^1_c}$	*trans*-$[\mathrm{Mo(CO)_4L^1_cL^2_t}]$
$[\mathrm{Mo(CO)_5L^2_t}]$	$\mathrm{L^2_t}$	*trans*-$[\mathrm{Mo(CO)_4(L^2_t)_2}]$
$[\mathrm{Mo(CO)_4(nbd)}]$	$\mathrm{L^1_c}$	*cis*-$[\mathrm{Mo(CO)_4(L^1_c)_2}]$
$[\mathrm{Mo(CO)_4(nbd)}]$	$\mathrm{L^1_t}$	
trans(*cis*)-$[\mathrm{Mo(CO)_4(L^1_c)_2}]$		*trans–cis*-$[\mathrm{Mo(CO)_4(L^1_c)_2}]$ (*ca.* 3 : 2)
trans-$[\mathrm{Mo(CO)_4(L^1_t)_2}]$		
trans–cis-$[\mathrm{Mo(CO)_4(L^1_c)_2}]$(3 : 2)	CO	$[\mathrm{Mo(CO)_5L^1_c}]$

As can be seen from Table 1, when $\mathrm{L_t}$ is involved, the thermal substitution reactions are highly stereoselective leading always to tetracarbonyl derivatives with the diazaphosphole ligands in mutual *trans* positions.* These results are in agreement with the observation that the norbornadiene ligand exchange route of $[\mathrm{Mo(CO)_4(nbd)}]$, in cyclohexane at room temperature, does not afford tetracarbonyl derivatives (*cis* or *trans*) on reaction with $\mathrm{L_t}$, whereas with $\mathrm{L^1_c}$ as entering ligand *cis*-$[\mathrm{Mo(CO)_4(L^1_c)_2}]$ is obtained. In addition, it has been found that *cis*(or *trans*)-$[\mathrm{Mo(CO)_4(L^1_c)_2}]$ thermally interconverts to *trans*(or *cis*)-$[\mathrm{Mo(CO)_4(L^1_c)_2}]$ to give an equilibrium composition in which the *trans* isomer predominates; on the other hand *trans*-$[\mathrm{Mo(CO)_4(L_t)_2}]$ does not undergo isomerization. In particular the thermal isomerization of *cis*-$[\mathrm{Mo(CO)_4(L^1_c)_2}]$ has been followed in a sealed n.m.r. tube in $\mathrm{CDCl_3}$ at 80 °C. A gradual disappearance of the methine signals of the *cis* derivatives was observed, with the concomitant appearance of the corresponding signals of the *trans* isomer. The equilibrium ratio *cis* : *trans* is about 2 : 3. Finally, when the thermal isomerization of $[\mathrm{Mo(CO)_4(L^1_c)_2}]$ is carried out in the presence of carbon monoxide, the corresponding pentacarbonyl $[\mathrm{Mo(CO)_5L^1_c}]$ is obtained in almost quantitative yield, thus suggesting a dissociative pathway.

TABLE 2

Infrared spectra in cyclohexane solutions

Compound	ν(CO)/cm^{-1}			
cis-$[\mathrm{Mo(CO)_4(L^1_c)_2}]$	2 020m	1 948m	1 928vs	1 921vs
trans-$[\mathrm{Mo(CO)_4(L^1_c)_2}]$	2 025w	1 975w	1 920s	
trans-$[\mathrm{Mo(CO)_4(L^1_t)_2}]$	2 045w	1 980w	1 925s	
trans-$[\mathrm{Mo(CO)_4L^1_cL^1_t}]$	2 040w	1 975w	1 910s	
cis-$[\mathrm{Cr(CO)_4(L^1_c)_2}]$	2 010m	1 942m	1 917s	1 910s
trans-$[\mathrm{Cr(CO)_4(L^1_c)_2}]$		1 960w	1 905vs	
trans-$[\mathrm{Cr(CO)_4(L^1_t)_2}]$	2 018w	1 950w	1 912s	
trans-$[\mathrm{Cr(CO)_4L^1_cL^1_t}]$	2 035w	1 965w	1 910s	
cis-$[\mathrm{W(CO)_4(L^1_c)_2}]$	2 020m	1 940m	1 915s	1 905vs
trans-$[\mathrm{W(CO)_4(L^1_c)_2}]$		1 980w	1 905vs	
trans-$[\mathrm{W(CO)_4(L^1_t)_2}]$	2 038w	1 965w	1 908s	
trans-$[\mathrm{W(CO)_4L^1_cL^1_t}]$	2 024w	1 975w	1 903s	
trans-$[\mathrm{Mo(CO)_4(L^2_t)_2}]$	2 038w	2 074w	1 920s	
trans-$[\mathrm{W(CO)_4L^1_tL^2_t}]$	2 038w	1 972w	1 918s	
trans-$[\mathrm{Mo(CO)_4L^1_cL^2_t}]$	2 035w	1 978w	1 910s	
trans-$[\mathrm{Mo(CO)_4(PPh_3)(L^1_t)}]$	2 020w	1 968w	1 902s	
trans-$[\mathrm{Mo(CO)_4(PPh_3)(L^1_c)}]$	2 020w	1 965w	1 900s	

TABLE 3

Physical properties and ^{1}H n.m.r. data [a]

Compound	Colour	M.p. (θ_c/°C)	δ(CH) [J(P–H)/Hz] [b]	δ($\mathrm{CH_2}$) [J(P–H)]
cis-$[\mathrm{Mo(CO)_4(L^1_c)_2}]$	White	198—200	5.35 (t, 9.5)	
trans-$[\mathrm{Mo(CO)_4(L^1_c)_2}]$	Cream	235—238	5.65 (t, 10.0)	
trans-$[\mathrm{Mo(CO)_4(L^1_t)_2}]$	White	160—163	4.75 (t, 4.0)	
trans-$[\mathrm{Mo(CO)_4L^1_cL^1_t}]$	Cream	170—175	4.81 (d, 4.0), 5.66 (m)	
cis-$[\mathrm{Cr(CO)_4(L^1_c)_2}]$	Cream	190—195	5.35 (t, 9.0)	
trans-$[\mathrm{Cr(CO)_4(L^1_c)_2}]$	Cream	215—220	5.60 (t, 9.5)	
trans-$[\mathrm{Cr(CO)_4(L^1_t)_2}]$	Cream	130—135	4.78 (t, 8.5)	
trans-$[\mathrm{Cr(CO)_4L^1_cL^1_t}]$	White	132—136	4.82 (m), 5.66 (m)	
cis-$[\mathrm{W(CO)_4(L^1_c)_2}]$	Yellow	200—205	5.45 (t, 9.0)	
trans-$[\mathrm{W(CO)_4(L^1_c)_2}]$	Yellow	241—245	5.87 (t, 10.0)	
trans-$[\mathrm{W(CO)_4(L^1_t)_2}]$	Yellow	200—205	4.73 (t, 7.5)	
trans-$[\mathrm{W(CO)_4L^1_cL^1_t}]$	Yellow	143—145	4.90 (d, 5.0), 5.90 (m)	
trans-$[\mathrm{Mo(CO)_4L^1_tL^2_t}]$	Cream	98—100	3.92 (d, 3.4), 4.66 (d, 4.5)	3.10—3.93 (m, AB)
trans-$[\mathrm{Mo(CO)_4(L^1_t)_2}]$	White	170—175	3.96 (t, 3.0)	3.04—4.03 (m, AB)
trans-$[\mathrm{Mo(CO)_4L^1_cL^2_t}]$	Cream	78—83	4.00 (d, 3.4), 4.59 (m)	3.17—3.98 (m, AB)
trans-$[\mathrm{Mo(CO)_4(PPh_3)(L^1_t)}]$	White	62—65	4.80 (d, 5.0)	
$\mathrm{L^1_c}$	White	183—185	5.49 (d, 21.3)	
$\mathrm{L^1_t}$	White	144—146	4.70 (d, 1.9)	
$\mathrm{L^2_t}$	White	112—114	3.94 (d, 2.0)	3.19—4.18 (m, AB)

[a] Run in $\mathrm{CDCl_3}$ solutions with $\mathrm{SiMe_4}$ as internal standard; the aromatic resonances are omitted. [b] Separation of the equally intense outer lines of the ' triplet '.

Spectral Data.—The results of i.r. analyses of the disubstituted metal carbonyls are collected in Table 2. Values for the metal carbonyl stretching frequencies correlate well with those for the analogous triphenylphosphine complexes.[5,6] The small differences observed in the ν(CO) i.r. absorptions in going from $[\mathrm{M(CO)_4(L^1_c)_2}]$ to $[\mathrm{M(CO)_4L^1_cL_t}]$ and to $[\mathrm{M(CO)_4(L_t)_2}]$ are an indication that different steric effects do not induce significant electronic effects in our disubstituted tetracarbonyl derivatives.

The ^{1}H n.m.r. data reported in Table 3 show that the methine protons of $\mathrm{L_c}$ and $\mathrm{L_t}$, both for the free and co-

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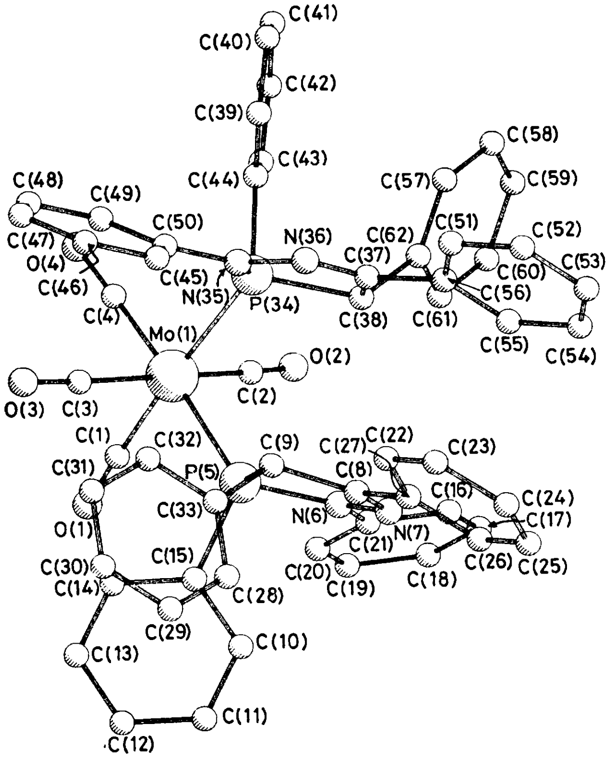
* It is possible that there are low percentages of the *cis* isomers $[\mathrm{M(CO)_4(L_t)_2}]$ and/or $[\mathrm{M(CO)_4L_cL_t}]$ present; however no clear evidence was found of the presence even in traces of these isomers by means of t.l.c., ^{1}H n.m.r. and i.r. spectroscopy.

ordinated ligands, exhibit distinctly different resonances which permit the identification of various complexes in the reaction mixtures. Thus the stereochemistry of the products can be easily determined by carrying out preliminary investigations in a sealed n.m.r. tube.

The importance of this diagnostic method becomes decisive when two different diasteroisomeric ligands are linked in mixed-phosphine tetracarbonyl complexes. In fact the methine proton of the co-ordinated *trans* and *cis* diazaphospholes gives signals in the range δ 3.92—4.90 and 5.35—5.90 p.p.m. respectively. As general features, these resonances are deshielded with respect to those of the unco-ordinated ligands, supporting their co-ordination through the phosphorus atom. In the case of *cis*-$[M(CO)_4(L^1{}_c)_2]$, the methine signals are shielded with respect to those of both the free and co-ordinated $L^1{}_c$ in the *trans*-$[M(CO)_4(L^1{}_c)_2]$ derivatives. As shown in Table 3, the benzylic protons of the co-ordinated $L^2{}_t$ appear as the AB portion of an ABX system ($X = {}^{31}P$).



Molecular structure of *cis*-$[M(CO)_4(L_c{}^1)_2]$

It is generally found that the proton n.m.r. spectra of disubstituted octahedral complexes with phosphines containing at least one alkyl group can be deceptively simple. Thus the complexes wherein the ligands are mutually *trans* exhibit apparent ' triplets ' of varying intensity ratios indicating P–P coupling, while the *cis* complexes exhibit apparent ' doublets ' indicating very small P–P coupling.[7] However, in our case, we observe that in both *cis*- and *trans*-$[M(CO)_4L_2]$ isomers the methine signals appear as more complicated ' triplets ' with different chemical shifts. Therefore in the disubstituted complexes described here, the above empirical correlation cannot be used for confirming the previous assignment of geometric isomerism.[8]

For obtaining an unequivocal assignment of the proposed geometry of the tetracarbonyl complexes, an *X*-ray determination was performed on *cis*-$[Mo(CO)_4(L^1{}_c)_2]$ which gave the most suitable crystals.

Molecular Structure of cis-$[Mo(CO)_4(L^1{}_c)_2]$.—The fractional atomic co-ordinates for the non-hydrogen atoms together with the estimated standard deviations are given in Table 4. The Figure shows the structure of the molecule. Thermal

TABLE 4

Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Mo	777(1)	2 277(1)	1 732(1)
C(1)	172(14)	2 335(15)	205(18)
C(1)	−216(11)	2 412(13)	−725(14)
C(2)	703(11)	3 724(15)	1 827(16)
O(2)	627(9)	4 568(11)	1 897(13)
C(3)	622(12)	815(15)	1 483(15)
O(3)	475(10)	12(11)	1 328(12)
C(4)	−321(12)	2 318(15)	2 291(18)
O(4)	999(9)	2 348(12)	2 586(15)
P(5)	2 162(3)	2 136(3)	961(4)
N(6)	2 801(9)	3 173(10)	1 069(12)
N(7)	3 646(8)	3 038(11)	1 462(13)
C(8)	3 806(11)	2 181(15)	1 787(14)
C(9)	3 094(10)	1 480(11)	1 748(14)
C(10)	2 800(7)	1 916(8)	−1 103(11)
C(11)	2 875(7)	1 423(8)	−2 141(11)
C(12)	2 337(7)	640(8)	−2 560(11)
C(13)	1 725(7)	350(8)	−1 940(11)
C(14)	1 650(7)	843(8)	−901(11)
C(15)	2 187(7)	1 626(8)	−483(11)
C(16)	2 995(7)	4 907(10)	1 152(10)
C(17)	2 738(7)	5 812(10)	782(10)
C(18)	2 022(7)	5 884(10)	−46(10)
C(19)	1 563(7)	5 050(10)	−503(10)
C(20)	1 820(7)	4 145(10)	−133(10)
C(21)	2 536(7)	4 073(10)	695(10)
C(22)	4 959(7)	1 207(8)	2 917(11)
C(23)	5 817(7)	1 034(8)	3 353(11)
C(24)	6 460(7)	1 643(8)	3 141(11)
C(25)	6 244(7)	2 424(8)	2 493(11)
C(26)	5 386(7)	2 597(8)	2 057(11)
C(27)	4 743(7)	1 988(8)	2 269(11)
C(28)	3 753(7)	250(8)	415(10)
C(29)	3 799(7)	−699(8)	−82(10)
C(30)	3 310(7)	−1 432(8)	229(10)
C(31)	2 775(7)	−1 216(8)	1 038(10)
C(32)	2 730(7)	−267(8)	1 536(10)
C(33)	3 219(7)	465(8)	1 224(10)
P(34)	1 596(3)	2 360(3)	3 695(4)
N(35)	2 164(9)	1 366(9)	4 166(11)
N(36)	3 017(9)	1 524(10)	4 079(12)
C(37)	3 243(10)	2 376(14)	4 632(14)
C(38)	2 652(9)	3 070(11)	4 013(15)
C(39)	1 244(6)	2 359(7)	5 889(9)
C(40)	858(6)	2 719(7)	6 807(9)
C(41)	266(6)	3 486(7)	6 701(9)
C(42)	61(6)	3 892(7)	5 679(9)
C(43)	447(6)	3 533(7)	4 762(9)
C(44)	1 039(6)	2 766(7)	4 867(9)
C(45)	2 406(5)	−382(8)	4 302(10)
C(46)	2 086(5)	−1 317(8)	4 302(10)
C(47)	1 200(5)	−1 463(8)	4 178(10)
C(48)	635(5)	−673(8)	4 054(10)
C(49)	955(5)	262(8)	4 054(10)
C(50)	1 841(5)	408(8)	4 178(10)
C(51)	4 604(9)	2 084(8)	5 911(11)
C(52)	5 457(9).	2 314(8)	6 346(11)
C(53)	5 842(9)	3 112(8)	5 998(11)
C(54)	5 375(9)	3 680(8)	5 215(11)
C(55)	4 522(9)	3 450(8)	4 780(11)
C(56)	4 137(9)	2 652(8)	5 128(11)
C(57)	2 561(8)	4 255(9)	5 766(10)
C(58)	2 403(8)	5 184(9)	6 253(10)
C(59)	2 200(8)	5 950(9)	5 579(10)
C(60)	2 155(8)	5 787(9)	4 417(10)
C(61)	2 314(8)	4 858(9)	3 931(10)
C(62)	2 517(8)	4 092(9)	4 605(10)

parameters and structure factor tables are in Supplementary Publication No. SUP 23025 (11 pp.).*

The *X*-ray study confirms that the *cis* diazaphosphole ligands are phosphorus bonded in *cis* positions, as suggested from i.r. analysis and from the ^{1}H n.m.r. chemical shifts of the methine protons. The structure of *cis*-$[Mo(CO)_4(L^1_c)_2]$ is that of a distorted octahedron, nevertheless it does retain approximate C_{2v} local symmetry and moreover the three mean planes defined by (*i*) C(1), C(4), Mo, P(5), and P(34); (*ii*) Mo, C(1), C(2), and C(3); (*iii*) Mo, C(2), C(3), and C(4) are approximately mutually perpendicular. The mean Mo–P distance, 2.506 Å, is significantly shorter than 2.71 Å, the sum of the covalent single bond radii (1.61 Å for molybdenum [9] and 1.10 Å for the phosphorus [10] atom) and falls within the narrow range (2.462—2 522 Å) found for the Mo–P bond in other tetracarbonyl complexes.[11-14] The relevant bond angles and bond lengths are collected in Table 5.

TABLE 5

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Mo–C(1)	1.95(1)	P(5)–N(6)	1.75(1)
Mo–C(2)	1.99(1)	P(5)–C(9)	1.88(1)
Mo–C(3)	2.03(1)	N(6)–N(7)	1.36(1)
Mo–C(4)	1.95(1)	N(7)–C(8)	1.29(1)
Mo–P(5)	2.496(3)	C(8)–C(9)	1.49(1)
Mo–P(34)	2.516(3)	P(34)–N(35)	1.713(9)
C(1)–C(1)	1.21(1)	P(34)–C(38)	1.92(1)
C(2)–C(2)	1.16(1)	N(35)–N(36)	1.41(1)
C(3)–O(3)	1.13(1)	N(36)–C(37)	1.25(1)
C(4)–O(4)	1.17(1)	C(37)–C(38)	1.49(1)
P(5)–C(15)	1.831(1)	P(34)–C(44)	1.821(7)
N(6)–C(21)	1.39(1)	N(35)–C(50)	1.43(1)
C(8)–C(27)	1.53(1)	C(37)–C(56)	1.48(1)

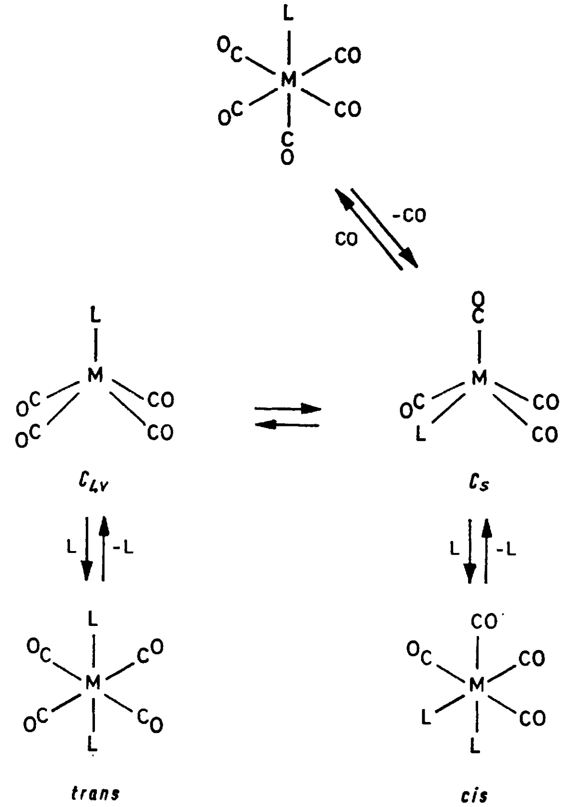
C(1)–Mo–C(2)	85.1(5)	Mo–P(5)–C(15)	120.7(3)
C(1)–Mo–C(3)	86.8(5)	Mo–P(5)–N(6)	118.4(3)
C(1)–Mo–C(4)	90.0(6)	Mo–P(5)–C(9)	118.8(4)
C(1)–Mo–P(5)	88.8(4)	N(6)–P(5)–C(9)	89.3(5)
C(1)–Mo–P(34)	174.8(4)	N(6)–N(7)–C(8)	112.5(9)
C(2)–Mo–C(3)	169.2(5)	P(5)–N(6)–N(7)	115.1(7)
C(2)–Mo–C(4)	86.5(5)	P(5)–C(9)–C(8)	101.7(7)
C(2)–Mo–P(5)	96.3(4)	N(7)–C(8)–C(9)	120.2(9)
C(2)–Mo–P(34)	90.0(3)	Mo–P(34)–N(35)	120.1(3)
C(3)–Mo–C(4)	86.4(5)	Mo–P(34)–C(44)	119.1(2)
C(3)–Mo–P(5)	90.6(3)	Mo–P(34)–C(38)	118.5(4)
C(3)–Mo–P(34)	98.3(3)	N(35)–P(34)–C(38)	87.7(4)
C(4)–Mo–P(5)	176.8(4)	P(34)–N(35)–N(36)	117.1(6)
C(4)–Mo–P(34)	91.5(4)	N(35)–N(36)–C(37)	110.6(9)
P(5)–Mo–P(34)	90.0(1)	N(36)–C(37)–C(38)	121.1(1.0)
O(1)–C(1)–Mo	177.1(1.2)	C(37)–C(38)–P(34)	102.2(7)
O(2)–C(2)–Mo	177.2(1.1)	O(3)–C(3)–Mo	175.2(1.1)
O(4)–C(4)–Mo	177.3(1.3)		

A comparison of the four Mo–C distances indicates that those of the axial atoms C(2) and C(3) are longer than those of the equatorial atoms C(1) and C(4); the mean bond lengths are 2.01 and 1.95 Å respectively and can be compared with Mo–C distances in other molybdenum–carbonyl complexes. In particular, the Mo–C axial and equatorial distances are very similar to those found for $[Mo(CO)_4(P_5Et_5)]$ [14] (2.01, 1.95 Å) and for $[Mo(CO)_4\{CH_2(PPh_2)\}]$ [13] (2.04, 1.93 Å). This shortening effect is a consequence of the poorer π-acceptor ability of the diazaphosphole ligands with respect to the CO group. The carbon–oxygen bond lengths are not significantly different, although the trend observed is that expected due to the complementary nature of the M–C and C–O bonds.

DISCUSSION

It is well known that the steric properties of phosphine ligands are difficult to change without altering their electronic properties [2,15,16] and that both these factors are important in determining the equilibrium composition of *cis* and *trans* tetracarbonyl complexes.[1]

In the present study the diastereoisomeric nature of the diazaphosphole ligands allowed us to explain the different stereochemical results only on the basis of steric effects. Our findings reported in Table 1 can be summarized as follows: (*i*) the reaction of $[Mo(CO)_4(nbd)]$ and L^1_t, carried out under mild conditions, does not produce the corresponding *cis* or *trans* tetracarbonyls, whereas L^1_c leads to the expected [17] *cis*-$[Mo(CO)_4(L^1_c)_2]$ complexes; (*ii*) when the bulkier ligand L_t is involved in the thermal substitution reactions, only the *trans* disubstituted tetracarbonyls are observed; (*iii*) the thermal isomerization of *trans*-$[Mo(CO)_4(L^1_t)_2]$ does not afford the corresponding *cis* isomer, whereas *trans*-$[Mo(CO)_4(L^1_c)_2]$ gives an equilibrium mixture of *cis* : *trans* (2 : 3).



SCHEME

There is much evidence [18,19] that square-pyramidal species such as $[M(CO)_4L]$ are intermediates in thermal and photochemical ligand substitutions in six-co-ordinate carbonyl derivatives; hence, the mechanism we propose involves the formation of an hypothetical unsaturated five-co-ordinate intermediate which may be fluxional [20] or rigid [2] on the time scale of the substitution reactions (Scheme).

It is predicted that, in d^6 square-pyramidal species,

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

weak π acceptors such as phosphines should show a preference for an equatorial site [21] and that steric effects also favour an equatorial position for bulkier ligands.[20] In both cases and when the reactions are carried out at low temperature, the C_s form may be rigid. This assumption would explain the exclusive formation of *cis*-$[Mo(CO)_4(L^1{}_c)_2]$ from reaction of $[Mo(CO)_4(nbd)]$ and $L^1{}_c$. Conversely, the non-formation of both *trans*- and *cis*-$[Mo(CO)_4(L^1{}_t)_2]$ when using the bulkier $L^1{}_t$ in the norbornadiene ligand exchange route may be due to a further stabilization of the C_s form and to steric repulsion between the co-ordinated and the incoming $L^1{}_t$ ligands.

When $[M(CO)_5L]$ undergoes thermal substitution at elevated temperatures (80—100 °C) where the higher energy form C_{4v} is now more accessible, the $C_s \rightleftharpoons C_{4v}$ isomerization takes place by a Berry type process.[22] Thus, addition of L to C_s will give *cis*-$[M(CO)_4L_2]$ while addition of L to C_{4v} will yield *trans*-$[M(CO)_4L_2]$; but if the incoming or bonded ligand L is L_t, the C_s form, probably for steric reasons, cannot give the *cis* tetracarbonyl derivatives and only the *trans*-$[M(CO)_4(L^1{}_t)_2]$ or *trans*-$[M(CO)_4L^1{}_cL_t]$, which are expected to be thermodynamically more stable, are obtained.

Finally the observed thermal isomerization reaction (shown below), which we have shown to proceed *via* a

$$cis\text{-}[Mo(CO)_4(L^1{}_c)_2] \rightleftharpoons trans\text{-}[Mo(CO)_4(L^1{}_c)_2]$$

dissociative pathway, can be explained by rearrangement of the, thus formed, C_s species to the C_{4v} form, prior to reaction with an incoming L_c ligand. For the steric reasons mentioned above, the isomerization of *trans*-$[Mo(CO)_4(L^1{}_t)_2]$ does not occur under similar conditions.

Although the results reported and discussed here do not present the kinetic aspects, we conclude that steric factors play an important role in determining the stereochemistry of disubstituted Group 6B tetracarbonyl derivatives. In addition, it is worthwhile to note that the particular nature of the diazaphosphole ligands allowed us to prepare and easily characterize mixed-phosphine complexes of the type *trans*-$[M(CO)_4L_tL]$ even with non-diastereoisomeric phosphines ($L = PPh_3$). Further investigations are underway in this direction and will be the object of future work.

EXPERIMENTAL

All reactions were carried out in an atmosphere of oxygen-free nitrogen. Solvents were distilled over sodium and then carefully purged with nitrogen before use. Infrared spectra were recorded on a Perkin-Elmer model 180 spectrometer using 0.5-mm cells; ^1H and ^{13}C n.m.r. spectra were recorded on a Varian XL 100, operating at 100 and 25.15 MHz respectively. Melting points are uncorrected. Diazaphosphole ligands L^1, L^2 and the complexes $[M(CO)_5L^1]$ were prepared as described previously.[3,4] The complex $[Mo(CO)_4(nbd)]$ was prepared according to literature methods.[23] Microanalyses were performed on pure complex isomers as well as on mixtures of isomers: the results obtained were practically identical. Column chromatography was performed with silica gel of particle size 0.05—0.2 mm. Infrared, ^1H n.m.r. data, and physical properties are collected in Tables 2 and 3. General methods are given below and some experimental details are summarized in Table 6.

Preparation of $[Mo(CO)_5L^2{}_t]$.—Equimolar amounts of $L^2{}_t$ (0.8 g, 2 mmol) and $[M(CO)_6]$ were refluxed in 200 cm³ of n-octane for *ca.* 8 h and the course of the reaction followed by t.l.c. After evaporation of the solvent, the reaction mixture was chromatographed on a silica gel column. Elution with a 35 : 2 : 1 mixture of n-hexane–benzene–diethyl ether gave the title complex (R_f 0.18) in 85% yield. Crystallization from CH_2Cl_2–n-pentane afforded white crystals with m.p. 107—110 °C (Found: C, 59.9; H, 3.55; N, 4.25. Calc. for $C_{32}H_{23}MoN_2O_5P$: C, 59.85; H, 3.60; N, 4.35%). I.r. ν(CO) (cyclohexane): 2 076s, 1 998m, 1 962s, 1 954s, 1 946s cm⁻¹; ^1H n.m.r. ($CDCl_3$) δ 3.98 [CH, d, *J*(P–H) 3.4 Hz], 3.19—4.03 (AB multiplet portion of ABX system, X = ^{31}P).

TABLE 6

Some experimental data

Complex [a]	M	Reaction time/h	Yield/ %	R_f [b]
cis-$[M(CO)_4(L^1{}_c)_2]$	Cr	7	25	0.15
	Mo	8	30	0.15
	W	14	23	0.15
trans-$[M(CO)_4(L^1{}_c)_2]$	Cr	7	38	0.10
	Mo	8	45	0.10
	W	14	35	0.10
trans-$[M(CO)_4(L^1{}_t)_2]$	Cr	40	80	0.03
	Mo	40	80	0.03
	W	60	80	0.03
trans-$[M(CO)_4L^1{}_cL^1{}_t]$	Cr	24	30	0.05
	Mo	40	40	0.05
	W	48	35	0.05
trans-$[M(CO)_4(L^2{}_t)_2]$	Mo	40	75	0.01
trans-$[M(CO)_4L^1{}_tL^2{}_t]$	Mo	40	40	0.02
trans-$[M(CO)_4L^1{}_cL^2{}_c]$	Mo	40	38	0.025

[a] Obtained as indicated in the experimental section and crystallized from CH_2Cl_2–n-pentanes. [b] Eluant: 35 : 2 : 1 solution of n-hexane–benzene–diethyl ether.

Preparation of $[M(CO)_4L_2]$ (M = Cr, Mo, *or* W; L = $L^1{}_c$, $L^1{}_t$, *or* $L^2{}_t$).—An iso-octane solution of $[M(CO)_5L^1{}_c]$ (2 mmol) was allowed to reflux for several hours in the presence of an equimolar amount of $L^1{}_c$ (0.784 g, 2 mmol) and the course of the reaction was conveniently followed by t.l.c. The reaction times were different depending on the nature of the metal carbonyl complexes. Chromatography of the resulting mixture on a silica gel column afforded *cis*-$[M(CO)_4(L^1{}_c)_2]$ and *trans*-$[M(CO)_4(L^1{}_c)_2]$. Following the same preparative route *trans*-$[M(CO)_4(L^1{}_t)_2]$ and *trans*-$[Mo(CO)_4(L^2{}_t)_2]$ were prepared by refluxing in iso-octane equimolar amounts of $[M(CO)_5L_t]$ and the corresponding *trans* diazaphosphole ligands $L^1{}_t$ or $L^2{}_t$. No formation of the *cis*-$[M(CO)_4(L_t)_2]$ isomer was observed in either case.

Analytical data for $[M(CO)_4(L^1)_2]$. Found: C, 70.9; H, 4.50; N, 5.85. Calc. for $C_{56}H_{42}CrN_4O_4P_2$: C, 70.9; H, 4.45; N, 6.00%. Found: C, 67.8; H, 4.30; N, 5.65. Calc. for $C_{56}H_{42}MoN_4O_4P_2$: C, 67.75; H, 4.25; N, 5.6%. Found: C, 62.5; H, 4.05; N, 5.10. Calc. for $C_{56}H_{42}N_4O_4P_2W$: C, 62.25; H, 3.90; N, 5.20%.

Analytical data for trans-$[Mo(CO)_4(L^2{}_t)_2]$. Found: C, 68.35; H, 4.40; N, 5.35. Calc. for $C_{52}H_{46}MoN_4O_4P_2$: C, 68.25; H, 4.55; N, 5.50%.

Preparation of trans-$[M(CO)_4LL^1{}_t]$ (M = Cr, Mo, *or* W;

$L = L^1_c$ *or* L^2_t).—A n-octane solution of $[M(CO)_5L^1_c]$ (6 mmol) was allowed to reflux for several hours in the presence of the *trans* ligand L^1_t, and the course of the reaction was conveniently followed by ^{1}H n.m.r. examination. Aliquots of the reaction mixture were removed at various time intervals, the solvent stripped off, and the residue dissolved in $CDCl_3$. Hydrogen-1 n.m.r. analysis of these samples revealed only a gradual increase of the characteristic signals of the methine protons of the title complex. At the end of the reaction the mixture was chromatographed on a silica gel column. Elution with the usual mixture of solvents gave pure *trans*-$[M(CO)_4L^1_cL^1_t]$. Very small amounts of $[M(CO)_5L^1_c]$, $[M(CO)_5L^1_t]$, *cis*-$[M(CO)_4(L^1_c)_2]$, and *trans*-$[M(CO)_4(L^1_t)_2]$ were detected as by-products by t.l.c. and their nature established by comparison of their i.r. and ^{1}H n.m.r. spectra with those of authentic samples. The same products distribution was obtained from the reaction of $[M(CO)_5L^1_t]$ and the *cis* ligand L^1_c. Similarly *trans*-$[Mo(CO)_4L^1_cL^2_t]$ and *trans*-$[Mo(CO)_4L^1L^2_t]$ were obtained and purified from mixtures containing the corresponding penta- and tetra-carbonyl by-products {Found: C, 67.9; H, 4.35; N, 5.50. Calc. for $[Mo(CO)_4L^1L^2_t]$, $C_{57}H_{44}MoN_4O_4P_2$: C, 68.0; H, 4.40; N, 5.55%}.

Reaction between $[Mo(CO)_4(nbd)]$ *and* L^1_c.—The complex $[Mo(CO)_4(nbd)]$ (0.14 g, 0.38 mmol) and L^1_c (0.30 g, 0.76 mmol) were stirred in cyclohexane at room temperature for *ca.* 6 h. The precipitate was filtered off and recrystallized from CH_2Cl_2–n-hexane to give *cis*-$[Mo(CO)_4(L^1_c)_2]$ in a 70% yield. The reaction of $[Mo(CO)_4(nbd)]$ and the *trans* ligand L^1_t did not afford the corresponding $[Mo(CO)_4(L^1_t)_2]$ tetracarbonyl even after longer reaction times.

Isomerization of cis-$[Mo(CO)_4(L^1_c)_2]$ *to trans*-$[Mo(CO)_4(L^1_c)_2]$.—The isomerization reaction of *cis*-$[Mo(CO)_4(L^1_c)_2]$ was carried out in $CDCl_3$ solution in a sealed n.m.r. tube which was placed in a constant-temperature bath at 80 °C. The *cis* $\rightleftharpoons$ *trans* isomerization was studied by observing the gradual decrease of the methine signals of the *cis* isomer (δ 5.35) and the concomitant increase of the methine signals of the *trans* complex (δ 5.65). After 4 h the signals ratio appeared to be constant with a proportion *cis* : *trans* of about 2 : 3. When the equilibrium mixture was placed in a carbon monoxide atmosphere under refluxing cyclohexane, a rapid reaction occurred and after *ca.* 2 h the exclusive formation of $[Mo(CO)_5L^1_c]$ and L^1_c was detected by t.l.c. A ^{13}C n.m.r. spectrum of the reaction mixture in $CDCl_3$ showed the usual pattern of CO signals: δ C_{trans} 208.3 [J(PC) = 30.3 Hz]; C_{cis} 204.6 [J(PC) = 9.3 Hz]. Under the same experimental conditions *trans*-$[Mo(CO)_4(L^1_t)_2]$ did not produce detectable amounts of the *cis* isomer, whereas under a carbon monoxide atmosphere the products $[Mo(CO)_5L^1_t]$ and L^1_t were observed by t.l.c. and the ^{13}C n.m.r. spectrum of the reaction mixture in $CDCl_3$ showed signals at δ C_{trans} 208.2 [J(PC) = 29.9 Hz], C_{cis} 203.8 [J(PC) = 29.9 Hz] which are attributable to the pentacarbonyl derivative.

X-Ray Data Collection and Structure Determination.—Suitable crystals of *cis*-$[Mo(CO)_4(L^1_c)_2]$ (m.p. 198—200 °C) were obtained by recrystallization from CH_2Cl_2–n-pentane. Intensity data were collected with a Philips PW1100 diffractometer using Mo-K_α (λ = 0.7107 Å) radiation in the range $3 \leqslant \theta \leqslant 25°$. Final crystal data are: $C_{56}H_{42}MoN_4O_4P_2$, M = 992.9, Triclinic, a = 15.728, b = 13.790, c = 12.109 Å, α = 95.17, β = 98.90, γ = 88.78°, U = 2 584.0 Å^3, Z = 2, D_c = 1.27 g cm^{-3}, $F(000)$ = 1 020, μ(Mo − K_α) = 3.09 cm^{-1}, space group $P\bar{1}$.

A Patterson synthesis and successive Fourier maps revealed all the non-hydrogen atoms. Of the 9 091 independent reflections, only the 3 117 having $I_o > 2.5\sigma(I_o)$ were used. The structure was refined by full-matrix least squares applying anisotropic temperature factors for carbonyl and diazaphosphole atoms; phenyl rings were refined as rigid groups. The function to be minimized was $\Sigma w[|F_o| - |F_c|]^2$ $\{w = 1.4108/[\sigma^2(F_o) + 0.004\,675(F_c)^2]\}$. The final conventional R index is 0.088. Throughout all calculations the SHELX system (G. M. Sheldrick, 1976) of programs was used. The drawings were obtained by PLUTO (W. D. S. Motherwell, 1976).

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