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SYNTHESIS OF MOLYBDENUM-RHODIUM BIMETALLIC COMPLEXES USING, AS LIGANDS, ELECTRON-RICH MOLYBDENUM(0) COMPLEXES CONTAINING AN η^6-METHYLDIPHENYLPHOSPHINE LIGAND

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Summary

The readily prepared complexes $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_2L$, (I), ($L = P(OMe)_3$ and $CNBu^t$) and $Mo(\eta^6\text{-}PhPMePh)(PPh_2CH_2CH_2PPh_2)L$, (II), ($L = PMePh_2$ and CO) react like tertiary phosphine ligands with $[RhCl(C_8H_{12})]_2$ to give the binuclear complexes $Mo(\eta^6\text{-}PhP_a\{RhCl(C_8H_{12})\}MePh)(PR_3)_2L$ ($PR_3 = PMePh_2$, III and $(PR_3)_2 = PPh_2CH_2CH_2PPh_2$, IV, respectively). Coordination of the rhodium at the η^6-phosphine phosphorus atom, P_a, is indicated in the ^{31}P NMR spectra of III and IV by the coupling $^1J(^{31}P_a, ^{103}Rh)$ and in the ^1H NMR by the inequivalence of the olefinic protons on the 1,5-cyclooctadiene (C_8H_{12}) ligand *trans* to P_a and Cl. Introduction of the rhodium centre perturbs only slightly the properties of complexes I and II except for complex I ($L = PMePh_2$) where extensive ligand exchange between the two metals occurs.

Introduction

There is much current interest in the synthesis of bimetallic complexes with the object of studying how reactions at one metal center are influenced by another metal held in close proximity [1]. An effective strategy for such syntheses is the use of metal complexes that are themselves phosphorus donor ligands. Recent examples include the low valent Group VI metal complexes $[\eta^6\text{-}C_6F_5PPh_2]Cr(\eta^6\text{-}C_6H_6)$ [2], $Li^+ [\eta^5\text{-}C_5H_4PPh_2]Mo(CO)_3^-$ [3], and $Li^+ [PPh_2]W(CO)_4(PPh_2H)^-$ [4] which serve as phosphine-like ligands in the synthesis of bimetallic complexes of Cr–Rh, Mo–Mn and W–Ir, respectively. These and related dinuclear complexes are being tested as catalysts for carbon monoxide reduction [3,4], olefin hydrogenation [2], hydroformylation [5], asymmetric hydrogenation [6], and other organic transformations [7,8].

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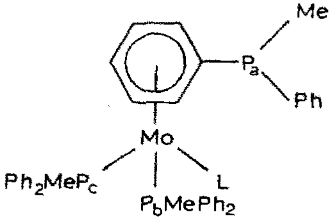
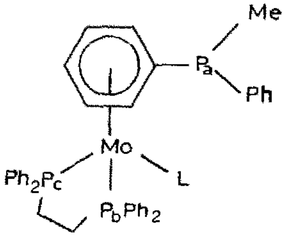
The phosphine-like complexes synthesized to date usually contain strongly coordinated, electron withdrawing ligands such as carbon monoxide. We are investigating the properties of a class of readily prepared complexes of molybdenum(0) with structures I and II containing an η^6-coordinated methyldiphenylphosphine ligand [9]. Such arene complexes are electron-rich and certain ones including Ia react readily with dinitrogen and dihydrogen [10]. Thus the use of complexes I and II as ligands is expected to result in reactive, electron rich bimetallic complexes.



(Ia, L = $PMePh_2$;
Ib, L = $P(OMe)_3$;
Ic, L = $CNBu^t$)



(IIa, L = $PMePh_2$;
IIb, L = CO)

The simple, high yield synthesis of complex Ia in one step from Mo_2Cl_{10} has been described previously [9]. A σ-bonded ligand in Ia is labile and can be substituted by a wide variety of small ligands, L, to give in high yield compounds that include Ib, L = $P(OMe)_3$ [9] and Ic, L = $CNBu^t$ [11]. The structure of Ic has been confirmed by X-ray diffraction [11]. Thus the influence of substitution at the molybdenum centre on the donor properties of the "dangling" phosphorus, P_a, can be systematically studied. We report here the preparation of two members of a new series of compounds Mo(η^6-PhPMePh)(DPPE)(L), (IIa), L = $PMePh_2$ and (IIb), L = CO, DPPE = $PPh_2CH_2CH_2PPh_2$, which allow further variation in the properties of these phosphine-like ligands. The ^1H and ^{31}P NMR spectra of these complexes are interesting because the chiral centre, P_a, places all the prochiral nuclei such as P_b and P_c in the molecules in different magnetic environments.

To demonstrate the utility of complexes I and II as ligands we have first made and characterized some molybdenum–rhodium dimeric compounds in which the coordination of the phosphorus donor is clearly indicated by $^{31}P-^{103}Rh$ coupling in the ^{31}P NMR spectra.

Discussion

The DPPE substituted molybdenum(0) complex IIa can be prepared in good yield (70–75%) either by a substitution reaction on Ia as in eq. 1 or by direct reduction under Ar of $MoCl_4(DPPE)$ with Mg in the presence of $PMePh_2$ (eq. 2). Complex IIa is isolated as a yellow-orange, air-sensitive solid.

$$\text{Ia} + \text{DPPE} \xrightarrow{\text{THF}} \text{IIa} + 2\,\text{PMePh}_2 \qquad (1)$$

$$\text{MoCl}_4(\text{DPPE}) + 2\,\text{PMePh}_2 + 2\text{Mg} \xrightarrow[\text{THF}]{\text{Ar}} \text{IIa} + 2\,\text{MgCl}_2 \qquad (2)$$

Confirmation of its structure comes from the ^{31}P NMR spectrum (Table 1) of IIa in C_6H_6 which shows the chiral "dangling" phosphorus P_a at -28.0 ppm as well as a σ-bonded $PMePh_2$ ligand, L, at 31.0 ppm coupled to two prochiral phosphorus atoms P_b at 85.8 ppm and P_c at 83.2 ppm. The ^1H NMR spectrum at 200 MHz (Table 2) displays five distinct multiplets at δ 3–5 due to inequivalent protons on the η^6-arene. Reaction 2 is yet another example of the formation of a π-bonded arylphosphine complex of molybdenum(0) from the reduction of molybdenum chloride species in the presence of four equivalents of the arylphosphine under Ar [9,12,13]. If the reduction is carried out under nitrogen then the dinitrogen complex $Mo(N_2)_2(DPPE)(PMePh_2)_2$ [14,15] is obtained in good yield.

Unlike complex Ia, complex IIa does not contain a very labile ligand. This is surprising considering the subtle structural differences between the two. Thus compound Ia reacts at 25°C in 20 min with 1 atm carbon monoxide to yield a monocarbonyl derivative [11] whereas IIa is only 80% converted to the monocarbonyl complex IIb after 72 h reaction at 66°C. The orange solid IIb has not been prepared free of starting complex IIa but does display a low carbonyl absorption in

TABLE 1

THE ^{31}P NMR DATA FOR COMPLEXES $Mo(\eta^6\text{-}PhP_aMePh)(L)(P_b)(P_c)$ AND $Mo(\eta^6\text{-}PhP_a(RhCl(COD))MePh)(L)(P_b)(P_c)$ IN C_6H_6 SOLUTION. REFERENCE DATA FOR SOME RHODIUM COMPLEXES V ARE ALSO INCLUDED (δ in ppm, J in Hz)

Complex	$\delta(P_a)$	$\delta(P_{calc})$ [a]	$^1J(P_a,Rh)$	$\delta(L)$	$\delta(P_b,P_c)$	$^2J(L,P_b$ or $P_c)$
$P_b,P_c = PMePh_2$						
Ib, L = $P(OMe)_3$	-27.9			176.3	40.2 [b]	52
					38.9 [b]	55
IIIb, L = $P(OMe)_3$	7.6	17.2	148	174.9	37.9	51
					37.8	51
Ic, L = $CNBu^t$	-24.2				38.4	
					38.3	
IIIc, L = $CNBu^t$	23.8	19.5	149		37.4	
					37.4	
$P_b + P_c = DPPE$						
IIa, L = $PMePh_2$	-28.0			31.0	85.8	25
					83.2	28
IVa, L = $PMePh_2$	8.0	17.1	147	25.3	85.3	28
					79.6	26
IIb, L = CO	-23.7				85.0 [b]	
					84.0 [b]	
IVb, L = CO	18.7	19.8	148		82.1	
					82.1	
RhCl(COD)P						
Va, P = $PMePh_2$	17.3	17.3	150			
Vb, P = PPh_3	30.8 [c]	30.8	152 [c]			
Vc, P = $P(OMe)_3$	122.0 [d]	122.0	249 [d]			

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[a] Calculated values for $\delta(P_a)$ of complexes III, IV and V are given by $\delta(P_{calc}) = 0.62\delta(P)+34.5$ where $\delta(P)$ is the chemical shift of the free tertiary phosphine. This equation is derived from the observed values of $\delta(P_a)$ from complexes V using the free ligand shifts $\delta(P) = -27.7$ for $PMePh_2$, -6.0 for PPh_3 and 140.7 ppm for $P(OMe)_3$. The shifts $\delta(P_a)$ of complexes I and II are used as $\delta(P)$ values for obtaining $\delta(P_{calc})$ for complexes III and IV, respectively. [b] These gave second order patterns that were analyzed from 81.0 MHz spectra: for Ib (an ABX pattern), $^2J(P_b,P_c)$ 31 Hz; for IIb, (an AB pattern), $^2J(P_b,P_c)$ 11 Hz; for the other complexes this ^2J coupling was not resolved. [c] Ref. 24. [d] Ref. 25.

TABLE 2

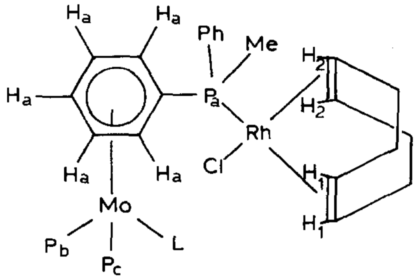
SOME ^1H NMR DATA [a] FOR THE COMPLEXES IN C_6D_6 (δ in ppm, J in Hz)

Complex	Phosphine methyl				Olefinic		η^6-Arene	Ligand L	
	$\delta(CH_3P_a)$	$J(P,H)$	$\delta(CH_3P_{b,c})$	$J(P,H)$	$\delta(H_1)$	$\delta(H_2)$	$\delta(H_a)$	$\delta(L)$	$J(P,H)$
Ib, L = P(OMe)$_3$	1.42	4	1.84 1.92	5 5			4.4,4.4 [b] 4.4,3.7 3.6	3.3	10
IIIb, L = P(OMe)$_3$	1.97	9	1.58 2.54	6 6	5.6	3.6	5.8,4.5 4.0,3.3 3.1	3.2	10
Ic, L = CNBu^t	1.50	4	1.61 1.77	5 5			3.7,4.0 4.1,4.2 4.3	1.40	
IIIc, L = CNBu^t	2.49	9	1.60 1.75	6 6	5.8	3.5	4.2,3.9 3.8,3.7 3.2	1.07	
			δCH_2P_b						
IIa, L = PMePh$_2$	1.27	4	2.1–2.5				4.9,4.5 4.0,3.7 3.1	1.43	5
IVa, L = PMePh$_2$	1.85	9	2.0–2.2		5.7	3.0	4.4,4.0 3.7,3.6 2.8	2.39	5
IIb, L = CO	1.46	4	2.0–2.2				5.0,4.7 4.5,4.1 3.9		
IVb, L = CO	2.00	9	2.1–2.3		5.8	3.5	5.2, 4.1 [b] 4.1, 3.8 3.0		
Va	2.05	9			5.6	3.1			

[a] Refer to the figures of the complexes I, II, III and IV for the labelling of atoms. Phenyl resonances at $\delta \sim 6.8$–8.0 and 1,5-cyclooctadiene resonances at δ 1.3–2.3 are not included. [b] Repeated values indicate superimposed resonances.

C_6H_6 at 1838 cm^{-1} consistent with its conjugation to a reduced metal centre. Its NMR data are listed in the Tables 1 and 2. We have not yet been able to prepare DPPE substituted analogues to Ib and Ic.

Complexes Ib, Ic, IIa and IIb react immediately with one half mole of $[RhCl(COD)]_2$, COD = 1,5-cyclooctadiene, in THF at 25°C under nitrogen to give the binuclear compounds IIIb, IIIc, IVa and IVb, respectively, that can be precipitated as analytically pure orange solids. The reaction with Ia is more complex (see below). Complexes III and IV as solids are oxidized by air only after several days but solutions decompose in minutes.



(III, IV)

(IIIb, P_c = P_b = $PMePh_2$, L = $P(OMe)_3$;
IIIc, P_c = P_b = $PMePh_2$, L = $CNBu^t$;
IVa, P_c + P_b = DPPE, L = $PMePh_2$;
IVb, P_c + P_b = DPPE, L = CO)

The coordination of the η^6-arylphosphine phosphorus P_a to the rhodium is indicated in the ^{31}P NMR spectra of compounds III and IV (Table 1) by couplings $^1J(^{31}P_a, ^{103}Rh) \sim 148$ Hz. The presence of five arene resonances H_a in the region 2.8–5.8 ppm in the ^1H NMR spectra (Table 2) demonstrates that the bridging ligand remains η^6-bonded to the molybdenum. These are clearly seen in the spectrum of complex IIIb, Fig. 1. The ^1H NMR spectra also show signals for the non-equivalent olefinic protons H_1 and H_2 on the cyclooctadiene ligands in III and IV and this is consistent with the square planar coordination geometry around the rhodium. The downfield resonance at $\delta \sim 5.7$ is assigned to H_1 *trans* to P_a consistent with previous assignments for the compounds [MCl(COD)L], M = Rh, Ir [16–20]. The resonance of H_2 which falls near arene resonances at $\delta \sim 3.5$ have been assigned by their larger peak integrations (two versus one for arene protons). The methyl proton resonance $\delta(CH_3P_a)$ shifts downfield and its coupling $^2J(P,H)$ increases in a characteristic fashion from 4 to 9 Hz upon complexation.

Complex Ia reacts with the rhodium complex to give a mixture of products. The main product accounting for greater than 70% of the total peak intensities in the ^{31}P NMR is $RhCl(PMePh_2)_3$ (see Experimental). Clearly extensive ligand exchange between the metal centres has occurred but the molybdenum containing species have not yet been identified or isolated. However work is in progress to study the nature of the ligand exchange processes in this and other bimetallic systems. The dramatic change in reactivity of Ia compared to the electronically very similar complexes Ib and IIa can be explained by the greater lability of the σ-bonded ligands in Ia.

Substitution of a phosphorus donor by a π-acid ligand in complexes I and II is expected to decrease the electron density and basicity of the "dangling" phosphorus atom P_a. The ^{31}P chemical shift of P_a which is sensitive to both the size and electronegativity of the substituents on P_a [21,22] appears to reflect the electronic effect since the resonances of the complexes containing π-acids, -24.2 (Ic) and

-23.7 ppm (IIb) fall downfield of that of free $PMePh_2$ (-27.7) whereas those of complexes containing three phosphorus σ-donors, -27.9 (Ib) and -28.0 ppm (IIa) are upfield. This trend is supported by data for a more extensive series of compounds [11].

The observed ^{31}P chemical shift of a phosphorus donor ligand in a complex, $\delta(P_a)$, is usually linearly related to the ^{31}P shift of the free ligand, $\delta(P)$ [21,23]. For the case of simple phosphorus ligands, P, in the complexes RhCl(COD)P, Va–Vc (Table 1) the relationship $\delta(P_{calc}) = 34.5 + 0.62\delta(P)$ reproduces observed $\delta(P_a)$ values. However this relationship does not accurately predict the chemical shifts for P_a in complexes III and IV possibly because of steric interactions between ligands on the two metals. The coupling constants $^1J(P_a,Rh) \sim 148$ Hz are relatively insensitive to substitution at the molybdenum.

A quantitative measure of the electronic properties of a phosphorus donor ligand, P, is given by the value of the $A_1\nu(CO)$ vibration of the complex $Ni(CO)_3P$ according to Tolman [22]. The synthesis of such metal carbonyl complexes using "ligands" I and II is complicated by ligand exchange between the metals [11]. However, an estimate of this parameter, ν, can be obtained from the chemical shifts of the olefinic protons H_1 in complexes III and IV since the linear relationship $\nu = 40\delta(H_1) + 1864$ has been demonstrated for $CDCl_3$ solutions of complexes IrCl(COD)P [18]. We have found that a similar equation $\nu = 67.5\delta(H_1) + 1700$ holds for complexes Va, Vb, Vd and Ve in $CDCl_3$ (see Experimental) but no good linear plot is obtained for C_6D_6 solutions; the best line parallel to the one for the $CDCl_3$ data is $\nu = 68\delta(H_1) + 1678$. The former equation cannot be applied to complexes III and IV since these compounds react immediately with chlorinated solvents; however the latter relationship and $\delta(H_1) = 5.7 \pm 1$ give an average value for complexes III and IV of $\nu = 2066 \pm 7$ cm^{-1}. Thus the phosphine-like complexes are electronically similar to $PMePh_2$ (ν 2067 cm^{-1}) in their donor properties as expected but the unpredictable solvent effects on $\delta(H_1)$ exerted by C_6D_6 or THF (also studied) did

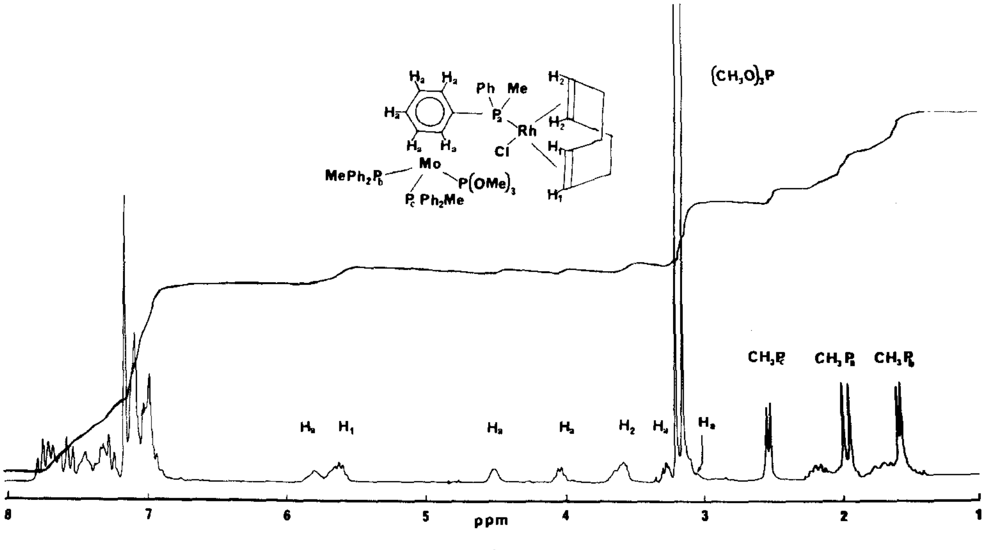


Fig. 1. The ^1H NMR spectrum at 200 MHz of $Mo(\eta^6\text{-}PhP(RhCl(COD))MePh)(PMePh_2)_2(P(OMe)_3)$ in C_6D_6.

not allow a comparison of donor properties to be made among complexes III and IV. Sterically these ligands are bulkier than $PMePh_2$ (cone angle 136° [22]) but a meaningful cone angle cannot be assigned to these very asymmetric phosphorus donor ligands.

There is no evidence for an interaction between the coordinatively unsaturated rhodium atom and the π-acid ligands on the molybdenum in IIIc and IVb since only minor perturbations to the isonitrile or carbonyl stretching frequencies of Ic, ν(CN) 1940 and IIb, ν(CO) 1838 cm^{-1}, respectively, are observed once these complexes are coordinated in IIIc (ν(CN) 1964 cm^{-1}) and IVb (ν(CO) 1835 cm^{-1}). In addition only minor shifts of ^1H and ^{31}P resonances of other ligands are observed upon coordination apart from the large chemical shift difference for the methyl protons on P_b (1.58 ppm) and P_c (2.54 ppm) in complex IIIb (Fig. 1) which appears to result from the rhodium complex enhancing the chiral environment about P_a.

In conclusion this work demonstrates the ease of preparation and modification of complexes that can be used as phosphorus-donor ligands and the ease of synthesis of molybdenum–rhodium dimeric complexes using them. Future work will address the nature of ligand exchange processes in dimeric compounds formed by these complexes and possible catalytic applications of bimetallics formed using these complexes.

Experimental

Oxygen and water were excluded during all operations by using vacuum lines or a glovebox supplied with purified nitrogen. Solvents other than methanol were dried over and distilled from sodium-benzophenone ketyl and were degassed before use. Methanol was dried over magnesium methoxide. The preparation and properties of the complex $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ (Ia) and its trimethyl phosphite and t-butylisonitrile derivatives (Ib and Ic) are reported elsewhere [9,11]. The literature method was used to prepare $[RhCl(COD)]_2$ [26]. A much higher yield (> 90%) of $MoCl_4$(DPPE) is obtained if the reaction time is increased to 1.5 h with the conditions reported [27].

The ^{31}P NMR spectra were recorded at 32.3 MHz with a Bruker WP80 spectrometer. Chemical shifts were measured relative to $P(OMe)_3$ in an insert tube but are reported relative to 85% H_3PO_4 with the use of $\delta(P(OMe)_3)$ + 140.7 ppm in C_6D_6. The data in ref. [9] for Ib differ from that in Table 1 because a less accurate reference value $\delta(P(OMe)_3)$ 139.8 ppm was used in the first report. The ^1H NMR spectra were obtained at 80 MHz using the WP80 or at 200 MHz using a Varian XL-200 spectrometer.

Microanalyses were performed on samples handled under an inert atmosphere by the Canadian Microanalytical Service and the results are listed in Table 3.

Preparation of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)(DPPE)$ *(IIa)*

(a) From $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ *(Ia).* Solid 1,2-bis(diphenylphosphino)ethane, (DPPE) (0.11 g, 0.28 mmol) was added to an orange solution of Ia (0.25 g, 0.28 mmol) in 15 ml THF. The resulting orange solution was concentrated to 5 ml after reacting for 30 min and treated with MeOH (10 ml) to yield the bright orange, air-sensitive, product (0.20 g, 76%).

(b) From $MoCl_4$*(DPPE).* The tetrachloride complex (1.62 g, 2.55 mmol) was

TABLE 3

ANALYTICAL DATA FOR THE COMPLEXES

Complex	Analyses (Found (calcd.) (%))		
	C	H	N
Ib	61.34 (61.47)	5.76 (5.90)	–
IIIb	55.54 (55.05)	5.86 (5.49)	–
Ic	67.74 (67.78)	6.24 (6.21)	1.75 (1.80)
IIIc	61.35 (60.86)	5.95 (5.89)	1.33 (1.36)
IIa	70.41 (69.80)	5.67 (5.63)	–
IVa	61.98 (63.14)	5.39 (5.47)	–
IVb	59.35 (59.49)	5.10 (5.10)	–

dissolved under argon in a solution of methyldiphenylphosphine (1.10 g, 5.49 mmol) in 75 ml of THF that was freshly dried and distilled from lithium aluminium hydride. Magnesium (2.0 g, 8.2 mmol), activated by exposure to iodine vapour, was then added. Nitrogen as well as oxygen and water must be rigorously excluded at this stage for a successful reaction; otherwise $Mo(N_2)_2(DPPE)(PMePh_2)_2$ [14,15] forms. The solution colour turned from red to green to brown to red-brown over a 30 min period during the reduction. After 2.5 h the magnesium was removed by filtration under argon, the filtrate was concentrated to 10 ml and the orange, oxygen sensitive product was precipitated with methanol. Recrystallization from benzene/MeOH and drying under vacuum gave the product (1.55 g, 68%).

Preparation of Mo(η^6-PhPMePh)(CO)(DPPE) (IIb)

Complex IIa (0.78 g, 0.88 mmol) was dissolved in 60 ml THF and then heated to reflux under an atmospheric pressure of carbon monoxide for 72 h. The solution was then concentrated to 5 ml and the product precipitated with methanol. Recrystallization from benzene/methanol gave an orange product (0.40 g, 64%) that consisted of an inseparable mixture of 80% IIb and 20% IIa (by ^{31}P NMR). IR (C_6H_6) 1838 cm^{-1} (ν(CO)). Treatment of this mixture with $[RhCl(COD)]_2$ allows the separation of pure IVb (see below).

Preparation of the bimetallic complexes III and IV

(a) Mo(η^6-PhP{RhCl(COD)}MePh)($PMePh_2)_2$(P(OMe)$_3$) (IIIb). A solution of the complex $[RhCl(COD)]_2$ (0.05 g, 0.09 mmol) dissolved in 5 ml THF was added dropwise over a 5 min period to a stirred solution of Mo(η^6-PhPMePh)-$(PMePh_2)_2(P(OMe)_3)$ (0.15 g, 0.18 mmol). After 30 min stirring, the solution was concentrated to 5 ml and the oxygen sensitive, orange-red product was precipitated with MeOH (5 ml), filtered, recrystallized from THF/methanol and dried under vacuum. Yield 0.12 g, 60%.

(b) $Mo(\eta^6\text{-}PhP\{RhCl(COD)\}MePh)(PMePh_2)_2(CNBu^t)$ *(IIIc).* A preparation identical to that for IIIb was employed. Yield 70%; orange solid. IR(benzene) 1964 cm^{-1} [ν(CN)].

(c) $Mo(\eta^6\text{-}PhP\{RhCl(COD)\}MePh)(DPPE)(PMePh_2)$ *(IVa).* The preparation as above gave orange crystals (70%).

(d) $Mo(\eta^6\text{-}PhP\{RhCl(COD)\}MePh)(DPPE)(CO)$ *(IVb).* The mixture containing IIb (0.09 g, 0.1 mmol IIb + 0.02 mmol IIa) was allowed to react with $[RhCl(COD)]_2$ (0.03 g, 0.06 mmol) as above. Only IVb precipitated as an orange solid (0.05 g, 50%) on careful addition of methanol. IR (benzene) 1833 cm^{-1} (ν(CO)).

Reaction of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ *(Ia) with* $[RhCl(COD)]_2$

Complex Ia (0.06 g, 0.07 mmol) and $[RhCl(COD)]_2$ (9 mg, 0.035 mmol) were added to benzene and the ^{31}P NMR spectrum was recorded after 1 h. The main product accounting for greater than 70% of the total peak intensity is $RhCl(PMePh_2)_3$ identified by equivalent *trans*-phosphines at δ 16.1 ppm, ^1J(P,Rh) 140 Hz coupled to one *cis*-phosphine at δ 31.2 ppm, ^1J(P,Rh) 184 Hz, ^2J(P,P) 42 Hz. These parameters match those of an authentic sample prepared as in ref. 28. Intractable mixtures precipitated from the reaction solution.

Observation of NMR spectra of $RhCl(COD)P$ *(V)*

The complexes Va, ($P = PMePh_2$), Vb ($P = PPh_3$) and Vd ($P = PCy_3$) were generated in NMR tubes in a glove box under N_2 by reacting $[RhCl(COD)]_2$ with the phosphine in a ratio P/Rh = 1.0 in the appropriate solvents [19,20]. The spectra of Vc ($P = P(OMe)_3$) [25] and Ve ($P = PPh_2Cl$) [19] have been reported. Some ^{31}P NMR data are listed in Table 1. ^1H NMR (C_6D_6, olefinic protons H_1 and H_2 respectively) δ: Va 5.57, 3.09; Vb 5.87, 3.20; Vc 5.83, 3.86; Vd 5.72, 3.62. ^1H NMR ($CDCl_3$, H_1 and H_2) δ: Va 5.55, 3.08; Vb 5.45, 3.11; Vd 5.27, 3.58; Ve 5.63, 3.93. Using the ν values (cm^{-1}) 2067.0 for $PMePh_2$, 2068.9 for PPh_3, 2079.5 for $P(OMe)_3$, 2056.4 for PCy_3 and 2080.7 for PPh_2Cl [22] the best line for the $CDCl_3$ data is $\nu = 67.5\delta(H_1) + 1700$ and for the C_6D_6 data is $\nu = 68\delta(H_1) + 1678$ cm^{-1}.

Acknowledgements

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