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Backbone modified small bite-angle diphosphines: Synthesis and molecular structures of $[M(CO)_4\{X_2PC(R^1R^2)PX_2\}]$ (M = Mo, W; X = Ph, Cy; R^1 = H, Me, Et, Pr, allyl, R^2 = Me, allyl)

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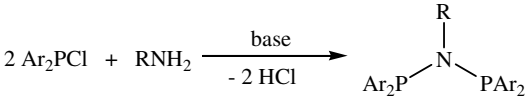
Abstract

A range of new small bite-angle diphosphine complexes, $[M(CO)_4\{X_2PC(R^1R^2)PX_2\}]$ (M = Mo, W; X = Ph, Cy; R^1 = H, Me, Et, Pr, allyl, R^2 = Me, allyl), have been prepared via elaboration of the methylene backbones in $[M(CO)_4(X_2PCH_2PX_2)]$ as a result of successive deprotonation and alkyl halide addition. When X = Ph it proved possible to replace both methylene protons but for X = Cy only one substitution proved possible. This is likely due to the electron-releasing nature of the cyclohexyl groups but may also be due to steric constraints. Attempts to prepare the bis(allyl) substituted complex $[Mo(CO)_4\{Ph_2PC(allyl)_2PPh_2\}]$ were only moderately successful. The crystal structures of nine of these complexes are presented.

Keywords: Diphosphine; Chelating; Dppm; Backbone modified; Molybdenum; Tungsten

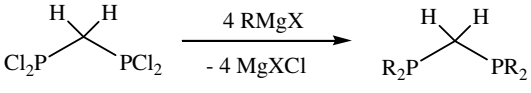
1. Introduction

Diphosphines are an important class of ligand that find widespread use in transition metal chemistry and catalysis. A subclass of these is small bite-angle diphosphines in which the two phosphorus centres are separated only by a single atom linker unit, the archetypal example being bis(diphenylphosphino)methane (dppm) [1–3]. Metal coordination of small bite-angle diphosphines has been shown to often lead to complexes that show unusual behaviour and recently this has been exploited with applications in a range of catalytic processes [4–24]. A wide range have been synthesised predominantly with carbon and nitrogen backbone atoms. Since the latter are prepared using primary amines as the source of the NR group (Eq. (1)) [25–40], a large number of backbone modified examples have been prepared, while phosphorus functionalisation appears to be limited to aryl groups.



(1)

In contrast, carbon-linked varieties are predominantly functionalised at phosphorus [41–57], with backbone functionalisation being far less widely studied [58–64]. This is due to the synthetic methods widely utilised (Eqs. (2)–(4)) since in all three the methylene backbone is a key component of one of the precursors.



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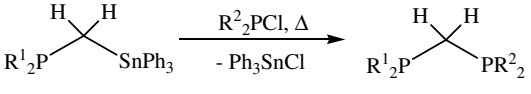

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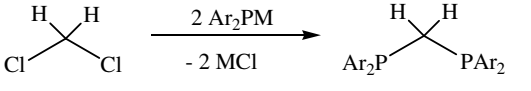

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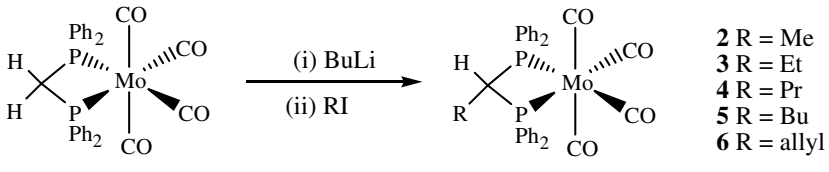
In theory, all three methods should be adaptable to give backbone substituted derivatives, however, in practice, backbone functionalised derivatives of $Cl_2PCH_2PCl_2$ and $R^1_2PCH_2SnPh_3$ are not known. Eq. (4) is potentially the most widely utilisable towards this aim since geminal dihalides can be readily prepared upon reduction of the corresponding aldehydes or ketones using PCl_5. Indeed, this route has been utilised towards the preparation of methyl substituted compounds, $Ph_2PCH(Me)PPh_2$ [58–61] and $Ph_2PC(Me)_2PPh_2$ [62]. However, even in these instances yields are relatively low when compared to the analogous synthesis of dppm via this method and a large number of side-products are observed by ^{31}P NMR spectroscopy. These possibly result from the competing reduction of the geminal dihalide and indeed this has been developed for the stereoselective reduction of geminal-dichlorocyclopropanes [65].

In the early 1980s, Shaw and co-workers developed an *on-metal* route to the backbone functionalisation of dppm [66–72]. This utilises the enhanced acidity of the methylene protons upon coordination of the diphosphine to a low-valent metal centre, those with electron-withdrawing ligands being particularly suitable. For example, they showed that addition of *n*-BuLi to $[Mo(CO)_4(dppm)]$ followed by treatment of the in situ generated anion with alkyl halides lead to the formation of backbone substituted derivatives $[Mo(CO)_4\{Ph_2PCH(R)PPh_2\}]$, and when excess MeLi was used as the base a double deprotonation can occur to afford $[Mo(CO)_4\{Ph_2PC(Me)_2PPh_2\}]$ after quenching with MeI. More recently we have adapted this procedure towards the *on-metal* backbone functionalisation of $(o\text{-tolyl})_2PCH_2P(o\text{-tolyl})_2$ [51]. In this case, only a single methylene proton can be replaced even under forcing conditions, an observation attributed to both the steric demands of the *ortho*-tolyl groups and also their better electron-releasing ability.

In a number of recent publications and patents, small bite-angle diphosphine complexes have been shown to be excellent catalysts for a number of different catalytic processes including the polymerisation and oligomerisation of ethylene [7,14], the selective co-trimerisation of ethylene and styrene co-monomers [8] and the asymmetric hydrogenation of a range of substrates [15,16]. A wide range of ligands have been used in these studies, however, for those based on a carbon backbone, while a number of phosphorus functionalised ligands have been tested, no attempt has yet been made to assess how steric and electronic changes to the backbone substituents might effect the performance of the catalyst. With this in mind, we decided to return to Shaw's *on-metal* backbone derivatisation studies of dppm with the aim of preparing hitherto unknown asymmetrically disubstituted derivatives, $Ph_2PC(R^1R^2)PPh_2$, and also to see if this methodology could be extended to the more basic bis(dicyclohexylphosphino)methane (dcpm).



1

2 R = Me
3 R = Et
4 R = Pr
5 R = Bu
6 R = allyl

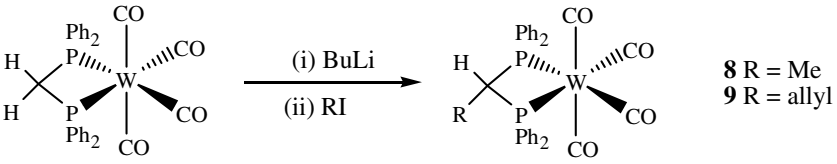
2. Results and discussion

2.1. Synthesis of mono-substituted complexes $[M(CO)_4\{Ph_2PCH(R)PPh_2\}]$ (2–9): structural characterisation of $[Mo(CO)_4\{Ph_2PCH(Pr)PPh_2\}]$ (4)

As detailed in the introduction, Shaw and co-workers have previously shown that $[Mo(CO)_4(dppm)]$ (**1**) can be readily deprotonated by *n*-BuLi, subsequent addition of alkyl halides leading to the formation of mono-substituted derivatives. In this way, $[Mo(CO)_4\{Ph_2PCH(Me)PPh_2\}]$ (**2**) can be prepared in moderate yields [66], being available in similar amounts upon addition of $Ph_2PCH(Me)PPh_2$ to *cis*-$[Mo(CO)_4(NHC_5H_{10})_2]$. In both cases the yields we recorded were for the recrystallised product and by ^{31}P NMR spectroscopy the reactions are essentially quantitative. Other mono-substituted complexes **3**–**6** were prepared analogously via the deprotonation method in crystalline yields of between 58% and 78%. Attempts to prepare **6** using allyl bromide gave poor yields, large amounts of **1** being reclaimed after work-up. We were also frustrated in trying to extend this simple methodology to bulkier alkyl iodides such as CyI, ^{i}PrI, ^{i}BuI and ^{t}BuI. In these cases, after work-up only **1** was reclaimed suggesting that either the anion generated is not nucleophilic enough to attack the sterically hindered and more electron-rich carbon centres or a competing elimination process simply regenerates the starting material. The tungsten complexes **8** and **9** were prepared in an analogous fashion from $[W(CO)_4(dppm)]$ (**7**) and were isolated in moderate crystalline yields.

All mono-substituted complexes are air-stable, pale yellow solids soluble in a range of organic solvents and characterisation was straightforward. They show three carbonyl absorptions in the IR spectrum, the positions of

which do not vary significantly with changes to the substituent. ^{31}P NMR spectroscopy is useful in assessing the conversion of the dppm complexes, substituent addition resulting in a downfield shift of the singlet resonance from 2.6 ppm in **1** to 22.6–25.6 ppm in **2–6**. In the ^{1}H NMR spectra, the characteristic triplet patterns shown by the methylene protons in **1** and **7** are replaced by a multiplet centred around a similar chemical shift range of δ 4.50–4.73.

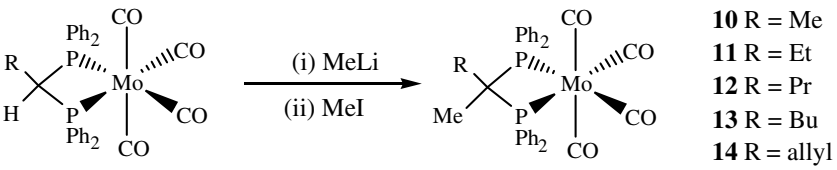


7

In order to probe the structural consequences of backbone substitution, the crystal structure of **4** was carried out (Fig. 1) in order to compare it with that of **1** which has previously been reported [73]. Key structural parameters are shown in Table 1. As expected, the backbone has been functionalized with a propyl group. In solution, this splits the four equivalent phenyl groups in **1** into two sets, while in the solid state all four are inequivalent. Addition of the propyl group to the backbone leads to a small increase in the P–C–P angle (ca. 0.7°) and concomitant decrease in the P–Mo–P bite-angle (ca. 0.5°), changes broadly consistent with an increased repulsion between the alkyl and diphenylphosphino groups. Molybdenum–phosphorus distances vary only slightly between **1** and **4**, as do the molybdenum–carbon distances to the carbonyls lying *cis* to the diphosphines. There is, however, a very marked difference in the molybdenum–carbon distances to the *trans* carbonyls which are elongated by an average of ca. 0.6 Å in **4** as compared to **1**. Since the same bonds in other substituted complexes (Table 1) are more in line with the values measured in **4** this difference may simply be a result of the relatively poor quality of the literature X-ray data for **1** [73].

*2.2. Synthesis of disubstituted complexes $[Mo(CO)_4\{Ph_2PCMe(R)PPh_2\}]$ (**10–14**), $[Mo(CO)_4\{Ph_2PC(allyl)_2PPh_2\}]$ (**15**) and $[W(CO)_4\{Ph_2PC(Me_2)PPh_2\}]$ (**16**): structural characterisation of **11–13***

Al-Jibori and Shaw have previously prepared $[Mo(CO)_4\{Ph_2PC(Me_2)PPh_2\}]$ (**10**) via the double deprotonation of **1** by MeLi followed by quenching with MeI [68]. One of our goals of this work was the preparation of unsymmetrically disubstituted complexes and with this in mind we followed a similar procedure starting with mono-alkyl-substituted **2–6** leading to the preparation of disubstituted complexes **11–14** in moderate crystalline yields. In all cases, addition of a slight excess of MeLi resulted in a darkening of the reaction solution which we associated with formation of the deprotonated species. However, no attempts were made to isolate these or characterise them in any way. Initially we stirred these solutions at room temperature for ca. 1 h in order to allow the reactions to proceed to completion. Subsequent addition of MeI then afforded the required unsymmetrically disubstituted complexes. However, by ^{31}P and ^{1}H NMR spectroscopy it was clear that under these conditions a mixture of three complexes resulted; namely the unreacted starting material, the expected product and the dimethyl-substituted complex **10**. Formation of the latter suggests that nucleophilic substitution of the methine proton may compete with deprotonation. We initially considered that the presence of starting mono-substituted complexes may result from their poor deprotonation; however, increasing the amount of MeLi or reaction time had little effect on its consumption. We then considered that the highly reactive nature of the generated anions, and their subsequent reaction with adventitious water, may be to blame. Consequently, addition of MeLi followed by almost immediate quenching with MeI was adopted. This indeed gave better conversion to the desired products and the sequence was sometimes repeated in order to enhance this conversion. We also attempted to prepare **11–13** from $[Mo(CO)_4\{Ph_2PCH(Me)PPh_2\}]$ (**2**) upon successive addition of MeLi and the required alkyl iodide. This was generally disappointing with only small amounts of the required disubstituted products being generated, even after successive additions. We attribute this to the relatively high reactivity of MeI as compared to other alkyl iodides.



2-6

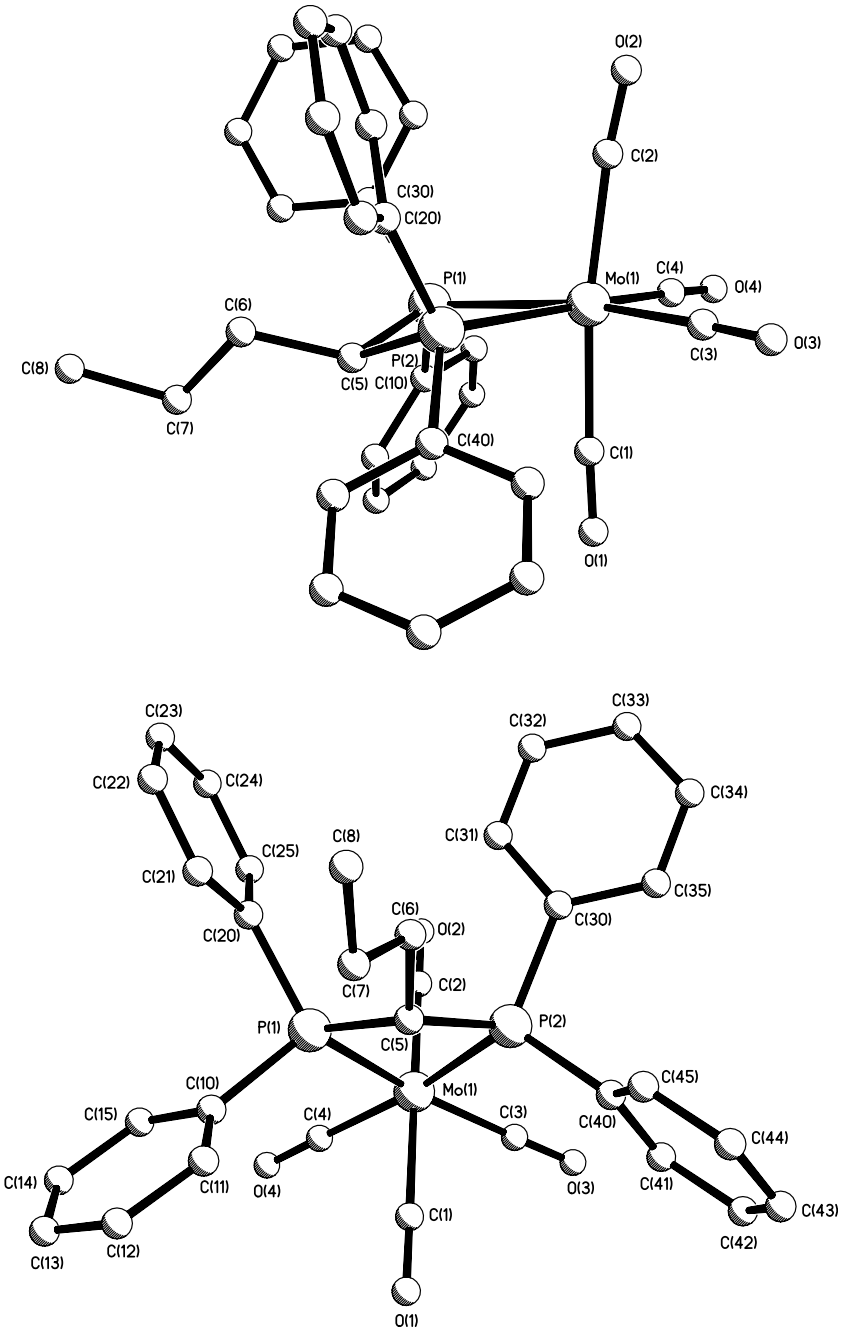
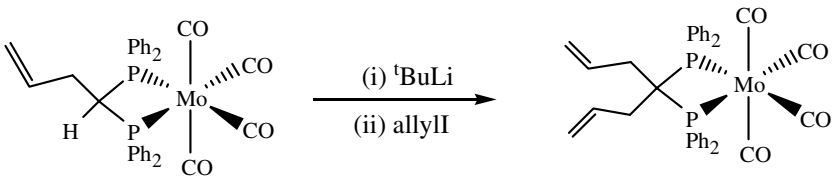


Fig. 1. Molecular structure and numbering scheme for $[Mo(CO)_4\{Ph_2PCH(Pr)PPh_2\}]$ (**4**) (hydrogen atoms omitted for clarity).

The allyl–methyl derivative **14** was produced upon deprotonation of **2** by MeLi followed by addition of excess allyl bromide. This method gave around 80% conversion of **2** in one-step, although a significant amount (ca. 10%) of the dimethyl complex **10** was also produced. Nevertheless, the relative success of the latter route spurred us on to attempt the synthesis of the diallyl complex $[Mo(CO)_4\{Ph_2PC(allyl)_2PPh_2\}]$ (**15**). The latter was a target for us as we hoped to be able to use a ring-closing metathesis route to prepare a diphosphine based on a cyclic backbone. Repeated deprotonation of $[Mo(CO)_4\{Ph_2PCH(allyl)PPh_2\}]$ (**6**) by ^{t}BuLi (MeLi was avoided since **14** would be a by-product) followed by addition of excess allyl iodide resulted in the slow generation of a new peak in the ^{31}P NMR spectrum at δ 49.9 being consistent with the formation of a disubstituted diphosphine. After eight successive deprotonation–quench cycles, conversion was around 66% by ^{31}P NMR. Unfortunately, we were unable to isolate a pure sample of **15** since all attempts to separate it from **6** were unsuccessful. Nevertheless, we are confident on the basis of spectroscopic data (see below) that this was formed.



6 **15**

All unsymmetrically disubstituted complexes are air-stable, pale yellow crystalline complexes with good solubility in a range of organic solvents. Their formation is easily shown by ^{31}P NMR spectroscopy, the observed singlet being shifted to ca. 25 ppm downfield of that observed in the analogous mono-substituted complexes. Again, IR spectra vary little from that of **1** and their mono-substituted precursors suggesting that even disubstitution of the backbone has little effect on the electron-donating nature of the diphosphine and the unsymmetrical nature of the backbone substitution leads to the maintained inequivalence of the phenyl groups above and below the MoPCP plane as easily seen by ^{1}H NMR spectroscopy. For the previously reported dimethyl complex, [Mo(CO)$_4${Ph$_2$PC(Me$_2$)PPh$_2$}] (**10**) [68], the methyl groups are equivalent and appear as a triplet at δ 1.46 ($J_{P-H} = 13.2$), while the aromatic region is also relatively simple due to the symmetrical nature of the diphosphine. For [Mo(CO)$_4${Ph$_2$PC(allyl)$_2$PPh$_2$}] (**15**), a similar equivalence of the two allyl groups is clearly seen in the ^{1}H NMR spectrum, with the appearance of resonances in the expected regions.

Crystallographic studies were carried out on three of these complexes, namely **11**–**13**, in order to compare the metric parameters with those of **1** and **4**, and also to assess the arrangement of the phenyl rings upon disubstitution. Data are summarized in Table 1, and the molecular structure of [Mo(CO)$_4${Ph$_2$PCMe(Et)PPh$_2$}] (**11**) as a representative example is shown in Fig. 2. Bond lengths in all three structures do not vary significantly from those found in **4**, nor do the observed P–Mo–P bite-angles of between 67.495(12)° and 67.941(12)°. As might be expected, however, the P–C–P angle is reduced upon disubstitution ranging from 94.50(6)° to 94.65(6)°, being around 1.7° smaller than that in **4**. This shows that while the addition of a second substituent has a marked effect on the angle at the diphosphine backbone this is not passed on to the metal centre,

Table 1
Selected bond lengths (Å) and angles (°) for [M(CO)$_4${X$_2$PC(R^{1}R^2)PX$_2$}]

	M–CO (*cis*) (Å)	M–CO (*trans*) (Å)	M–P (Å)	P–M–P (°)	P–C–P (°)
[Mo(CO)$_4$(Ph$_2$PCH$_2$PPh$_2$)][a]	2.07(1)	1.92(1)	2.501(2)	67.3(1)	95.6(4)
	2.02(2)	1.94(1)	2.535(3)		
[Mo(CO)$_4${Ph$_2$PCH(Pr)PPh$_2$}] (**4**)	2.0328(15)	1.9807(14)	2.4954(3)	67.829(11)	96.29(6)
	2.0485(15)	2.0010(15)	2.5132(3)		
[Mo(CO)$_4${Ph$_2$PCMe(Et)PPh$_2$}] (**11**)	2.0310(14)	1.9907(15)	2.5132(4)	67.941(12)	94.50(6)
	2.0349(15)	1.9976(15)	2.5185(4)		
[Mo(CO)$_4${Ph$_2$PCMe(Pr)PPh$_2$}] (**12**)	2.0292(16)	1.9833(16)	2.5024(4)	67.495(12)	94.60(6)
	2.0379(16)	1.9937(15)	2.5395(4)		
[Mo(CO)$_4${Ph$_2$PCMe(allyl)PPh$_2$}] (**13**)	2.029(2)	1.993(2)	2.5070(5)	67.917(16)	94.65(8)
	2.038(2)	1.998(2)	2.5289(5)		
[Mo(CO)$_4$(Cy$_2$PCH$_2$PCy$_2$)] (**17**)	2.027(2)	1.985(2)	2.5241(5)	67.397(17)	98.81(10)
	2.041(2)	1.989(2)	2.5410(5)		
[W(CO)$_4$(Cy$_2$PCH$_2$PCy$_2$)] (**18**)	2.025(3)	1.987(3)	2.5187(6)	67.20(2)	98.21(13)
	2.036(3)	1.988(3)	2.5324(6)		
[Mo(CO)$_4${Cy$_2$PCH(Me)PCy$_2$}] (**19**)	2.025(3)	1.993(3)	2.5187(7)	67.95(2)	97.61(12)
	2.040(3)	1.995(3)	2.5207(7)		
[Mo(CO)$_4${Cy$_2$PCH(Et)PCy$_2$}] (**20**)	2.020(3)	1.986(2)	2.5338(6)	67.06(3)	97.12(14)
	2.030(3)	1.986(2)			
[Mo(CO)$_4${Cy$_2$PCH(allyl)PCy$_2$}] (**21**)	2.030(2)	1.990(2)	2.5214(5)	67.804(16)	98.66(6)
	2.032(2)	1.997(2)	2.5453(5)		
[Mo(CO)$_4${(*o*-tolyl)$_2$PCH$_2$P(*o*-tolyl)$_2$}][b]	2.028(5)	1.979(4)	2.5338(11)	67.20(3)	99.2(2)
	2.051(5)	1.981(5)	2.5561(10)		
[Mo(CO)$_4${(*o*-tolyl)$_2$PCH(Me)P(*o*-tolyl)$_2$}][b]	1.993(8)	1.972(5)	2.5502(12)	67.66(5)	97.6(3)
	2.042(8)	1.972(5)	2.5502(12)		
[Mo(CO)$_4${(*o*-tolyl)$_2$PCH(Bz)P(*o*-tolyl)$_2$}][b]	2.021(3)	1.963(4)	2.5378(8)	66.58(3)	96.33(13)
	2.031(4)	1.990(3)	2.5767(9)		

[a] Reference [73].
[b] Reference [51].

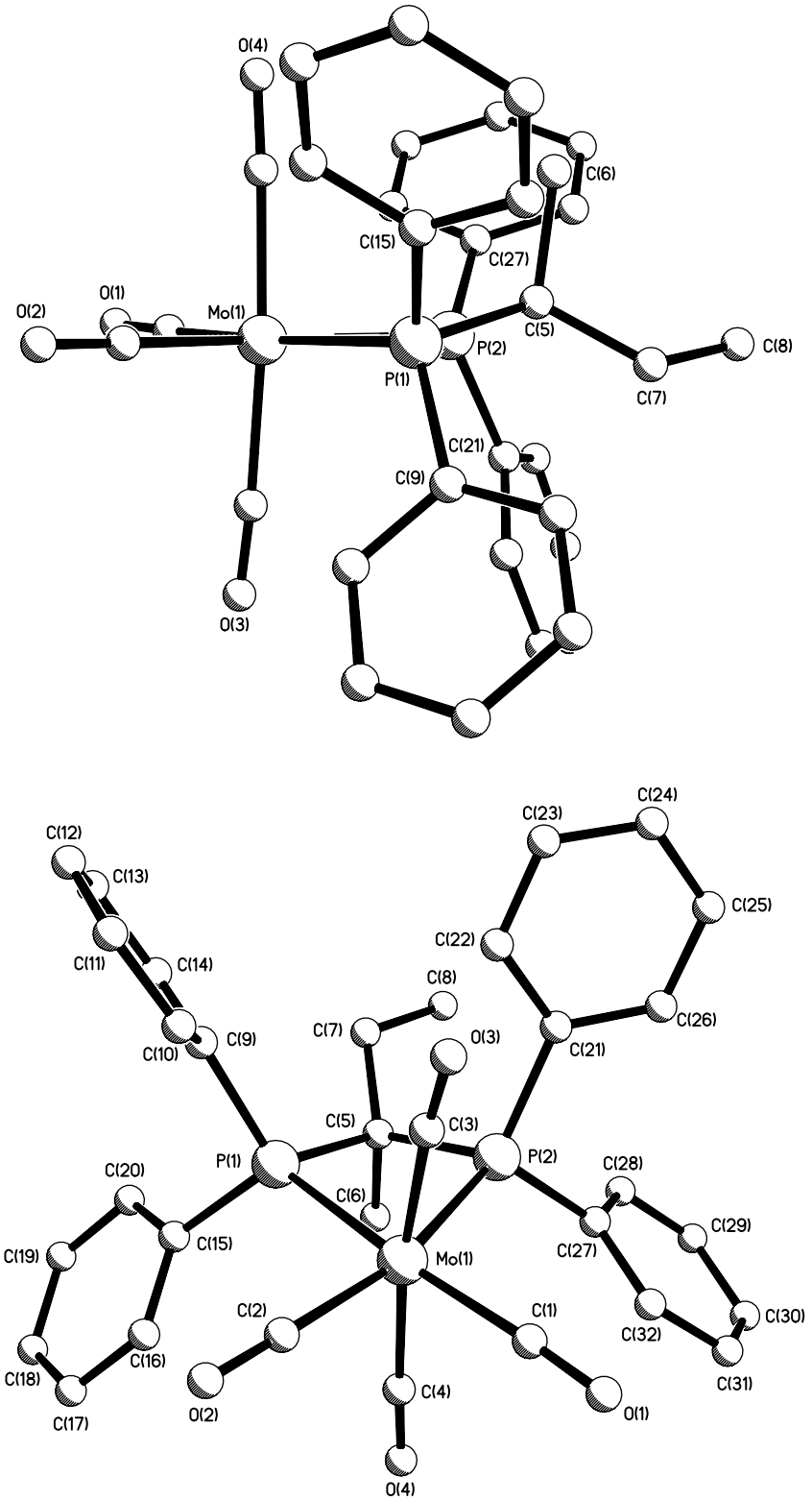
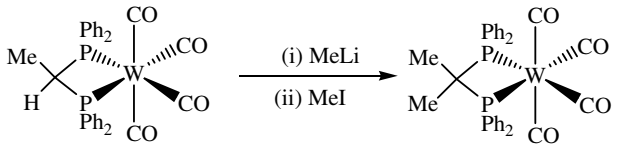


Fig. 2. Molecular structure and numbering scheme for $[Mo(CO)_4\{Ph_2PCMe(Et)PPh_2\}]$ (**11**) (hydrogen atoms omitted for clarity).

presumably due to the flexibility of the Mo–P–C angles. The orientation of the phenyl groups is very similar in all three complexes **11**–**13**, and also bears a close resemblance to that found in **4**. Thus, one of the groups [C(9)–C(14) in **11**] is rotated significantly with respect to the other three, lying approximately perpendicular to them and this group always lies on the same side of the diphosphine as the longest of the backbone substituents.

As alluded to above, the known tungsten dimethyl complex **16** [68] was easily prepared in high yield (94%) upon

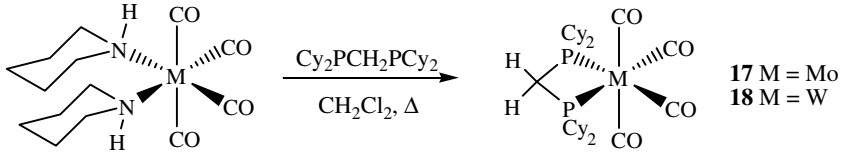
deprotonation of **8** by MeLi followed by quenching with MeI. An attempt was also made to prepare the diallyl-substituted $[W(CO)_4\{Ph_2PC(allyl)_2PPh_2\}]$ via deprotonation of the mono-allyl complex **9** followed by addition of allyl bromide. While some evidence was gleaned for the generation of the latter, the use of MeLi as the deprotonating agent (see above) was unfortunate and lead to the formation of a mixture containing methyl-substituted products along with the desired diallyl derivative. Further attempts to prepare the diallyl complex using ^{t}BuLi as a base are currently in progress.



8 **16**

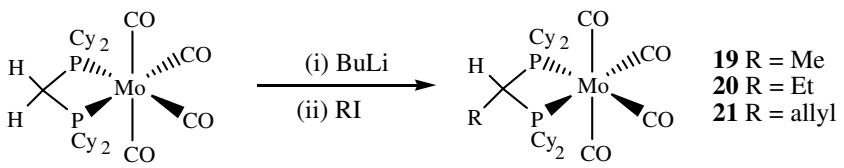
2.3. Synthesis and structural characterisation of cyclohexyl-substituted complexes $[M(CO)_4\{Cy_2PCH(R)PCy_2\}]$ (**16–20**)

The coordination chemistry of bis(dicyclohexylphosphino)methane (dcpm) has been explored to a far lesser extent than that of the related bis(diphenylphosphino)methane (dppm) [46,74–80]. This is in part to its more challenging synthesis and air sensitivity in solution. As far as we are aware, backbone-functionalised derivatives of dcpm are currently unknown. They should be available via the method developed by Rothwell and co-workers for the catalytic hydrogenation of arylphosphines using for example, $Ph_2PCH(Me)PPh_2$ or $Ph_2PC(Me_2)PPh_2$ as starting materials. We were interested to see if Shaw's methodology, to date only applied to dppm, could be extended to this more bulky and electron-donating diphosphine. Somewhat surprisingly, we could not find reference to the synthesis of any of the group VI tetracarbonyl complexes of dcpm so consequently we initially prepared $[Mo(CO)_4(dcpm)]$ (**17**) and $[W(CO)_4(dcpm)]$ (**18**) in moderate isolated yields upon thermolysis of the free ligand and *cis*-$[M(CO)_4(NHC_5H_{10})_2]$ in dichloromethane. Both are easily characterised, IR spectra showing the characteristic tetracarbonyl pattern being shifted by around 12–15 cm^{-1} to lower wavenumbers as compared to the analogous dppm complexes, a result of the more electron-releasing nature of the alkyl phosphines.



The molecular structures of both **17** and **18** were investigated by X-ray crystallography. The complexes are isostructural (Table 2). Data are summarized in Table 1 and the molecular structure of $[Mo(CO)_4(dcpm)]$ (**17**) is shown in Fig. 3. Few significant differences are seen between the structure of **17** and that of the related phenyl-functionalised complexes. For example, the bite-angle of the diphosphine at 67.397(17)° is indistinguishable from that found in **1**, although as might be expected, the P–C–P angle of 98.81(10)° is over 3° larger than that found in **1**. A noteworthy feature of the orientation of the cyclohexyl rings is that they those on either phosphorus atom lie approximately perpendicular to one another while on either side of the diphosphine pairs of cyclohexyl groups are approximately parallel. This suggests that the greatest steric interaction between cyclohexyl rings is between those on the same phosphorus atom.

In order to prepare the first examples of backbone functionalised dcpm ligands we treated **17** sequentially with *n*-BuLi and RI leading to formation the new diphosphine complexes **19–21** in moderate crystalline yields. Formation of **19** and **20** proceeded relatively straightforwardly, but conversion of **17** to **21** was less efficient and the procedure was repeated twice in order to generate significant product. All display very similar spectroscopic properties to **17**, the remaining methine proton appearing as a multiplet at between δ 3.18 and 3.47.



17

The crystal structures of all three new molybdenum complexes were carried out (Table 1) and the molecular structure of $[Mo(CO)_4\{Cy_2PCH(allyl)PCy_2\}]$ **21** as a

Table 2
Crystal data and collection and refinement details for new complexes

Compound	**4**	**11**	**12**	**13**	**17**	**18**	**19**	**20**	**21**
Empirical formula	$C_{32}H_{28}MoO_4P_2$	$C_{32}H_{28}MoO_4P_2$	$C_{33}H_{30}MoO_4P_2$	$C_{33}H_{28}MoO_4P_2$	$C_{29}H_{46}MoO_4P_2$	$C_{29}H_{46}WO_4P_2$	$C_{123}H_{188}Mo_4O_{19}P_8$	$C_{31}H_{50}MoO_4P_2$	$C_{32}H_{50}MoO_4P_2$
Formula weight	634.42	634.42	648.45	646.43	616.54	704.45	2602.25	644.59	656.60
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	*Pbca*	*Pbca*	$P2_1/c$	$P2_1/m$	$P2_1/c$
Temperature (K)	293(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
a (Å)	9.4418(6)	12.1290(6)	17.8552(12)	11.8877(11)	18.3477(13)	18.3539(11)	18.7960(13)	8.7614(7)	11.3002(9)
b (Å)	17.3456(11)	13.7921(7)	9.6650(6)	13.9578(13)	15.5405(11)	15.4842(9)	15.8810(11)	20.7393(15)	16.5626(13)
c (Å)	18.3159(11)	18.0899(10)	19.4329(13)	18.6855(18)	21.3580(15)	21.3638(12)	21.9585(16)	9.6466(7)	17.1139(13)
β(°)	100.731(1)	104.982(1)	114.159(1)	107.163(1)	90	90	101.677(1)	113.424(1)	94.743(1)
Volume (Å^3)	2932.1(3)	2923.3(3)	3059.8(3)	2962.3(5)	6089.9(7)	6071.5(6)	6418.9(8)	1608.4(2)	3192.1(4)
Z	4	4	4	4	8	8	2	2	4
D_{calc} (Mg m^{-1})	1.437	1.442	1.408	1.449	1.345	1.541	1.346	1.331	1.336
F(000)	1296	1296	1328	1320	2592	2848	2732	680	1384
Crystal size (mm)	$0.34 \times 0.28 \times 0.16$	$0.28 \times 0.28 \times 0.26$	$0.28 \times 0.26 \times 0.15$	$0.28 \times 0.24 \times 0.04$	$0.28 \times 0.14 \times 0.12$	$0.38 \times 0.20 \times 0.20$	$0.36 \times 0.30 \times 0.16$	$0.26 \times 0.18 \times 0.16$	$0.26 \times 0.18 \times 0.17$
θ Range (°)	1.63–28.30	1.74–28.28	2.12–28.29	1.85–28.30	1.92–28.26	1.91–28.33	1.69–28.30	1.96–28.28	1.71–28.27
Reflections collected	25346	25127	26117	25319	50988	50714	54803	14204	27570
Independent reflections (R_{int})	6993 (0.0158)	6933 (0.0138)	7319 (0.0174)	7040 (0.0190)	7427 (0.0331)	7397 (0.0242)	15279 (0.0258)	3958 (0.0204)	7645 (0.0198)
Data/restraints/ parameters	6993/0/352	6933/1/352	7319/0/361	7040/0/361	7427/0/325	7397/0/325	15279/0/678	3958/0/187	7645/0/352
Goodness-of-fit on F^2	1.045	1.056	1.035	1.127	1.041	1.072	1.019	1.033	1.074
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0218$, $wR_2 = 0.0559$	$R_1 = 0.0232$, $wR_2 = 0.0593$	$R_1 = 0.0249$, $wR_2 = 0.0631$	$R_1 = 0.0298$, $wR_2 = 0.0752$	$R_1 = 0.0345$, $wR_2 = 0.0825$	$R_1 = 0.0248$, $wR_2 = 0.0307$	$R_1 = 0.0457$, $wR_2 = 0.1214$	$R_1 = 0.0377$, $wR_2 = 0.0933$	$R_1 = 0.0312$, $wR_2 = 0.0813$
Largest difference in peak and hole (e Å^{-3})	0.409 and −0.220	0.658 and −0.288	0.492 and −0.337	0.626 and −0.585	0.845 and −0.429	1.387 and −0.491	1.856 and −0.788	0.802 and −0.631	1.588 and −0.510

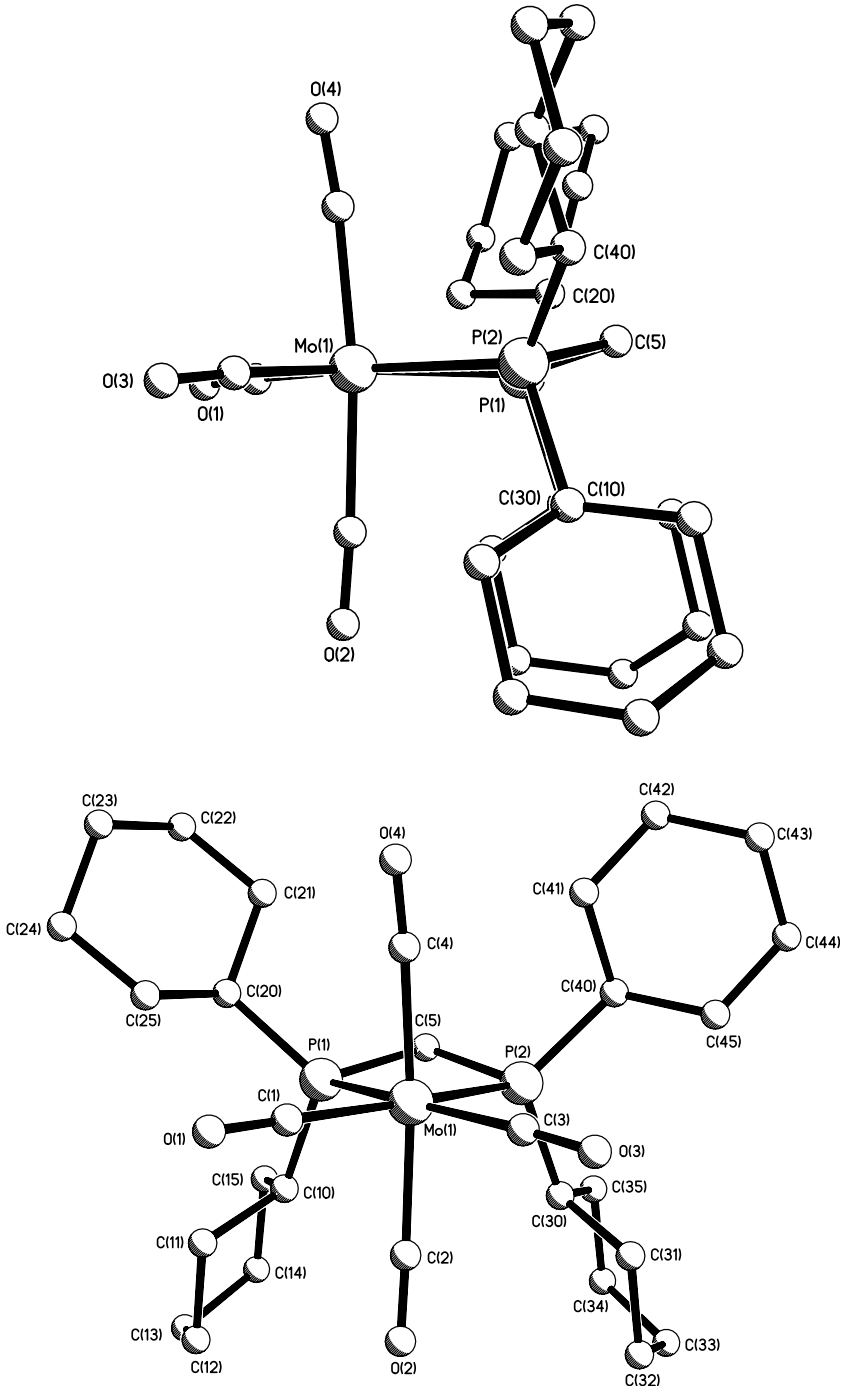


Fig. 3. Molecular structure and numbering scheme for $[Mo(CO)_4(dcpm)]$ (**17**) (hydrogen atoms omitted for clarity).

representative example is shown in Fig. 4. Introduction of the substituent leads to no significant changes in bond lengths and angles as compared to **17** with P–C–P and P–Mo–P angles over the three structures lying on either side of those found in **17**. In **19** and **20** the observed relative orientations of the cyclohexyl groups is maintained (it is crystallographically imposed in **20** as a result of the mirror plane that includes the metal, backbone carbon and *cis* carbonyls), however, in **21** it is somewhat different being more randomly orientated.

Repeated attempts to add a second substituent to the backbone of dcpm met only with failure. A range of bases were attempted but all failed to result in significant deprotonation as evidenced by the high yield of starting materials reclaimed. We attribute this to the decreasing acidity of the remaining backbone proton and also to steric difficulties for the addition of the incoming electrophile. Thus it seems that at the molybdenum carbonyl stabilized centre the dcpm cannot be further functionalized. As alluded to above, such ligands should be

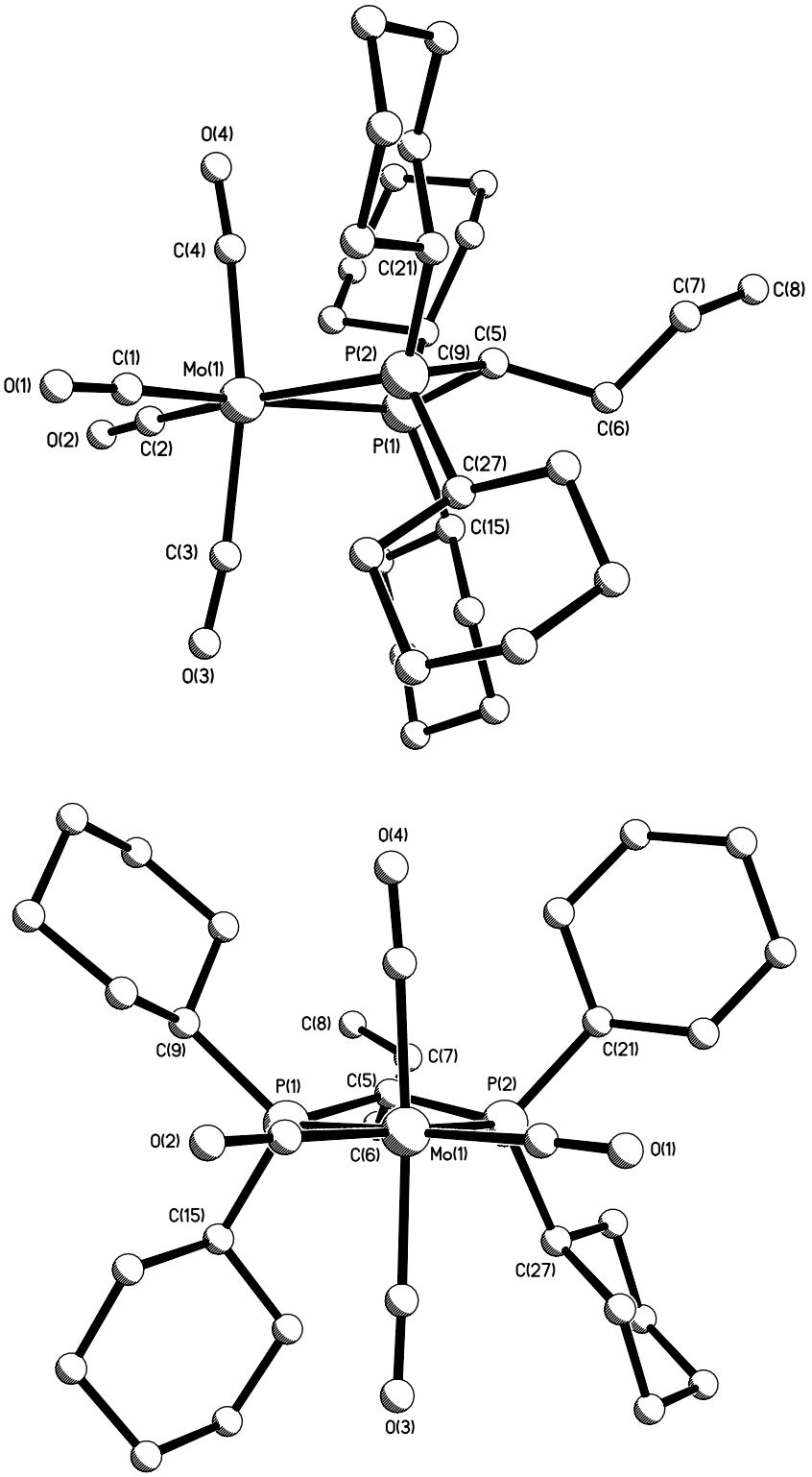


Fig. 4. Molecular structure and numbering scheme for $[Mo(CO)_4\{Cy_2PCH(allyl)PCy_2\}]$ (**21**) (hydrogen atoms omitted for clarity).

accessible upon hydrogenation of $Ph_2PC(R_2)PPh_2$ or perhaps via the double deprotonation of more electron-deficient dcpm complexes, and with this in mind we are currently investigating the reactivity of the diborane complex of dcpm.

3. Conclusions

This contribution has developed work previously reported by Shaw and co-workers [66–72], showing that the backbone of the readily available small bite-angle

diphosphine dppm can be readily modified when coordinated to the molybdenum and tungsten tetracarbonyl centres. Importantly, asymmetric disubstituted complexes unavailable via standard methods can be prepared in this manner. The diphosphines bind strongly to the low-valent centres and appear to be indefinitely stable both in the solid state and solution. Infra-red spectra suggest that backbone functionalisation does not significantly affect the donor properties of the diphosphine but the introduction of steric bulk at this position should have a significant effect on the stability of chelate *versus* bridge coordination modes, while also restricting the rotation about the P–Ar bonds and thus allowing a more well-defined coordination environment about the metal centre. While we have not shown the latter directly here we have previously demonstrated this for related *ortho*-tolyl diphosphines [51]. We have also shown for the first time that the more basic dcpm ligand can also be backbone modified, although somewhat disappointingly addition of only a single substituent appears to be possible. This is likely due to the more basic nature of this ligand but also to the enhanced steric bulk at phosphorus and corresponds with the situation found for the *ortho*-tolyl derivative where again only a single substituent could be added [51]. The high stability of the prepared complexes suggests that these ligands will bind strongly to a wide-range of low-valent metal centres and thus may have applications in homogeneous catalysis. No attempts were made to liberate the free diphosphines from their group VI complexes. This is likely only to be achievable under highly oxidising conditions, which would almost certainly lead to the oxidation (or destruction) of the diphosphines. A goal of our work is the preparation of the free diphosphines and with this in mind we are now developing related chemistry of the borane-protected diphosphines. These are easily prepared from the diphosphine and $BH_3 \cdot thf$ and the strong Lewis acidity of the borane group should render the backbone protons acidic and thus susceptible to substitution. Unlike the low-valent metal centre, the borane unit is easily removed upon addition of excess base and this route should allow preparation of the free diphosphines. Studies in this area are ongoing and will be reported in due course.

4. Experimental

All reactions were carried out under a nitrogen atmosphere in dried degassed solvents unless otherwise stated. *cis*-$[M(CO)_4(NHC_5H_{10})_2]$ (M = Mo, W) and $[M(CO)_4$-(dppm)] (M = Mo, W) [81,82] were prepared by the literature method and bis(dicyclohexylphosphino)methane was purchased from Aldrich and used as supplied. NMR spectra were run on a Bruker AMX400 spectrometer and referenced internally to the residual solvent peak (^1H) or externally to $P(OMe)_3$ (^{31}P). Infrared spectra were run on Nicolet 205 or Shimadzu 8700 FT-IR spectrometers in a solution cell fitted with calcium fluoride plates, subtraction of the solvent absorptions being achieved by computation. Fast atom bombardment mass spectra were recorded on a VG ZAB-SE high resolution mass spectrometer and elemental analyses were performed in house.

Synthesis of $Ph_2PCH(Me)PPh_2$. 1,1-Dibromoethane (2.15 ml, 0.025 mol) was added dropwise to the stirred solution of $LiPPh_2$ (ca. 0.05 mol) under nitrogen leading to a colour change from red to yellow. After stirring for 1 h, methanol (ca. 20 ml) was added, the solution was transferred to a round bottom flask and volatiles were removed by rotary evaporation to a give yellow-grey solid. This was dissolved in dichloromethane (ca. 100 ml) and washed with water (3 × 50 ml). The dichloromethane solution was dried with magnesium sulphate, filtered and volatiles were removed under reduced pressure to leave a crude orange product. This was washed with a small amount of ethanol to give a fine white powder. Crystallisation upon adding ethanol to a concentrated dichloromethane solution gave $Ph_2PCH(Me)PPh_2$ as a fine white solid (4.48 g, 45%). ^1H NMR ($CDCl_3$) δ 7.54–7.27 (m, 20H, Ph), 3.21 (q, $J = 6.94$, 1H, CH), 1.01 (dt, $J = 10.3$, $J = 7.01$, 3H, Me); ^{31}P NMR ($CDCl_3$) δ −6.5 (s).

Synthesis of $Ph_2PC(Me_2)PPh_2$. A thf (10 ml) solution of 2,2-dichloropropane (5.64 g, 0.05 mol) was added to a stirred solution of $LiPPh_2$ (ca. 0.10 mol) in thf (150 ml). After stirring overnight the solution turned from deep red to orange and upon addition of methanol (ca. 10 ml) the solution turned straw yellow. After removal of volatiles under reduced pressure, the dry solid was dissolved in dichloromethane (ca. 100 ml) and washed with water (3 × 50 ml). After drying the dichloromethane portion with magnesium sulphate, removal of volatiles gave an orange oil. This was washed with a small amount of ethanol to give a white precipitate (7.59 g, 39% yield). ^1H NMR ($CDCl_3$) δ 7.8–7.4 (m, 20H, Ph), 1.25 (t, $J = 10.3$, 6H, 2Me); ^{31}P NMR ($CDCl_3$) δ 12.8 (s).

*Synthesis of $[Mo(CO)_4\{Ph_2PCH(Me)PPh_2\}]$ (**2**).* $[Mo(CO)_4(NHC_5H_{10})_2]$ (1.00 g, 2.64 mmol) and Ph_2PCH-$(Me)PPh_2$ (1.05 g, 2.64 mmol) were refluxed in dichloromethane (40 ml) for 1 h. The solution was filtered and concentrated on a rotary evaporator and crystals were obtained upon adding methanol and placing the mixture in a freezer overnight. More crystals were obtained by concentrating the reaction solution and placing back in the freezer. Total yield: 0.61 g (40%). Alternatively, **1** (0.43 g, 0.72 mmol) was dissolved in toluene (20 ml) and TMEDA (0.16 ml, 1.08 mmol) and *n*-BuLi (0.43 ml, 1.08 mmol) were added causing the solution to turn from yellow to dark red-orange. This was stirred for 1 h, MeI (0.089 ml, 1.44 mmol) was added and the mixture was stirred overnight. The solution turned cloudy yellow-brown and volatiles were removed to give a grey-brown solid. This was dissolved in dichloromethane (ca. 20 ml) and washed with water (3 × 30 ml). The dichloromethane portion was dried over magnesium sulphate and concentrated on a rotary evaporator. Methanol was added and the solution was placed in a freezer to give pale yellow crystals (0.34 g, 77%).^1H NMR ($CDCl_3$) δ 7.61–7.35 (m, 20H, Ph), 4.70 (m, 1H, CH), 1.15 (dt, $J = 13.0$, $J = 7.6$, 3H, Me); ^{31}P NMR

($CDCl_3$) δ 22.6 (s). Anal. Calc. for **2**: C, 57.42, H, 4.67. Found: C, 57.54, H, 3.86%. IR ν(CO) (CH_2Cl_2) 2020s, 1907s, 1882s cm^{-1}.

*Synthesis of [Mo(CO)$_4${Ph$_2$PCH(Et)PPh$_2$}] (**3**).* To **1** (0.18 g, 0.30 mmol) in thf (40 ml) was added TMEDA (0.07 ml, 0.51 mmol) and *n*-BuLi in hexane solution (0.3 ml, 0.75 mmol). The solution turned orange and was then stirred for 1 h before EtI (0.18 g, 1.17 mmol) was added and the mixture left stirring overnight. Removal of volatiles gave an oily solid which was dissolved in dichloromethane (30 ml) and washed with water (3×40 ml). The dichloromethane portion was then dried over magnesium sulphate, filtered and concentrated under vacuum. Methanol was added to give pale yellow crystals (0.11 g, 58%). ^{1}H NMR ($CDCl_3$) δ 7.60–7.36 (m, 20H, Ph), 4.52 (m, 1H, CH), 1.54 (m, 2H, CH_2), 0.77 (t, $J = 7.3$, 3H, Me); ^{31}P NMR ($CDCl_3$) δ 24.7 (s); IR ν(CO) (CH_2Cl_2) 2019s, 1905s, 1878s cm^{-1}.

*Synthesis of [Mo(CO)$_4${Ph$_2$PCH(Pr)PPh$_2$}] (**4**).* To **1** (0.41 g, 0.69 mmol) in thf (30 ml) was added *n*-BuLi (0.55 ml, 1.40 mmol) resulting in a colour change from light yellow to dark brown-orange. This was stirred for 30 min and PrI (2.65 ml, 0.26 mmol) was added. The mixture was left to stir overnight forming a dark brown solution. Removal of volatiles gave an oily solid that was dissolved in dichloromethane (30 ml), washed with water (3×40 ml) and dried with magnesium sulphate. Removal of volatiles gave a yellow-brown solid which was dissolved in the minimum amount of dichloromethane and layered with methanol to give crystals (0.31 g, 72%). ^{1}H NMR ($CDCl_3$) δ 7.53–7.25 (m, 20H, Ph), 4.60 (tt, $J = 10.8$, 6.8, 1H, CH), 1.45 (m, 2H, CH_2), 1.20 (sextet, $J = 7.9$, 2H, CH_2), 0.61 (t, $J = 7.3$, 3H, Me); ^{31}P NMR ($CDCl_3$) δ 25.1 (s); IR ν(CO) (CH_2Cl_2) 2019s, 1906s, 1881s cm^{-1}. Anal. Calc. for **4**: C, 60.57, H, 4.45. Found: C, 59.16, H, 4.37%.

*Synthesis of [Mo(CO)$_4${Ph$_2$PCH(Bu)PPh$_2$}] (**5**).* To **1** (0.41 g, 0.69 mmol) in thf (40 ml) was added *n*-BuLi (0.55 ml, 1.40 mmol). This was stirred for 30 min and then BuI (0.30 ml, 2.68 mmol) was added and the solution was allowed to stir overnight turning dark brown. Removal of volatiles gave a solid which was dissolved in dichloromethane (40 ml) and washed with water (3×30 ml). The dichloromethane portion was dried with magnesium sulphate and pumped down. Crystals were obtained by dissolving the washed and pumped down solid in the minimum amount of dichloromethane and adding a little methanol (0.33 g, 73%). ^{1}H NMR ($CDCl_3$) δ 7.52–7.36 (m, 20H, Ph), 4.60 (m, 1H, CH), 1.45 (m, 2H, CH_2), 1.12 (quintet, $J = 7.3$, 2H, CH_2), 0.97 (sextet, $J = 7.3$, 2H, CH_2), 0.59 (t, $J = 7.3$, 3H, Me); ^{31}P NMR ($CDCl_3$) δ 25.1 (s); IR ν(CO) (CH_2Cl_2) 2018s, 1906s, 1881s cm^{-1}. Anal. Calc. for **5**: C, 61.12, H, 4.66. Found: C, 60.58, H, 4.76%. Mass spectrum (FAB): m/z 650 (M^+), 592 (M^+-2CO), 538, (M^+-4CO).

*Synthesis of [Mo(CO)$_4${Ph$_2$PCH(allyl)PPh$_2$}] (**6**).* To **1** (0.23 g, 0.39 mmol) in thf (50 ml) was added *n*-BuLi (0.50 ml, 2.80 mmol). The solution turned dark orange and was stirred for 2 min. Allyl iodide (1.02 ml, 11.2 mmol) was then added causing another colour change to dark brown-orange. This was stirred for 15 min and then volatiles were removed under vacuum leaving a viscous brown-orange oil. This was dissolved in dichloromethane (50 ml) and washed with water (3×40 ml). The dichloromethane portion was then dried over magnesium sulphate and filtered. Orange crystals were obtained by layering a concentrated solution of the product in dichloromethane with methanol and leaving the solution to mix slowly (0.19 g, 78%). ^{1}H NMR ($CDCl_3$) δ 7.65–7.25 (m, 20H, Ph), 5.40 (qt, $J = 10.1$, 6.9, 1H, CH), 4.90 (dd, $J = 10.1$, 1.1, 1H, $=CH_2$), 4.73 (dd, $J = 18.4$, 1.1, 1H, $=CH_2$), 4.67 (m, 1H, PCHP), 2.24 (m, 2H, CH_2); ^{31}P NMR ($CDCl_3$) δ 25.6 (s); IR ν(CO) (CH_2Cl_2) 2019s, 1908s, 1884s cm^{-1}.

*Synthesis of [W(CO)$_4${Ph$_2$PCH(allyl)PPh$_2$}] (**9**).* To **7** (0.21 g, 0.31 mmol) in thf (20 ml) was added *n*-BuLi (0.62 ml, 1.5 mmol) in hexane, the solution turning dark orange. This was stirred for 15 min and allyl bromide (0.16 ml, 1.8 mmol) was added. After 2 h removal of volatiles under vacuum gave an orange solid. This solid was dissolved in dichloromethane (20 ml), washed with water (3×30 ml), dried with magnesium sulphate and filtered. This solution was concentrated under vacuum and layered with methanol. Slow mixing of the solvents yielded crystals (0.98 g, 89%). ^{1}H NMR ($CDCl_3$) δ 7.71–7.38 (m, 20H, Ph), 5.5 (m, 1H, CH), 5.03 (d, $J = 10.5$, 1H, CH_2), 4.73 (d, $J = 17.5$, 1H, CH_2), 2.19 (m, 2H, CH_2); ^{31}P NMR ($CDCl_3$) δ 1.1 (s, $J_{W-P} = 102.4$); IR ν(CO) (CH_2Cl_2) 2015s, 1897s, 1878s cm^{-1}.

*Synthesis of [Mo(CO)$_4${Ph$_2$PC(Me)$_2$PPh$_2$}] (**10**) [68].* [$Mo(CO)_4(NHC_5H_{10})_2$] (1.048 g, 2.72 mmol) and $Ph_2PC(Me)_2PPh_2$ (1.165 g, 2.82 mmol) were refluxed in dichloromethane (40 ml) for 1 h. The solution was then allowed to cool before being filtered. It was then concentrated on a rotary evaporator before adding methanol and placing the mixture in a freezer overnight to obtain **10** as yellow crystals (0.25 g, 16%). Alternatively, to **2** (0.26 g, 0.43 mmol) in thf (20 ml) was added MeLi (1.35 ml, 2.17 mmol) causing the solution to turn from yellow to dark red-orange. This was stirred for 1 h before adding MeI (0.13 ml, 2.17 mmol) which caused an immediate colour change to brown-orange. After stirring overnight, volatiles were removed under vacuum to leave a dark brown-orange solid. This was dissolved in dichloromethane (20 ml) and washed with water (3×30 ml). The dichloromethane solution was then over magnesium sulphate and filtered. The solution was then concentrated on a rotary evaporator before adding methanol and placing the mixture in the freezer to obtain crystals (0.24 g, 89%). ^{1}H NMR ($CDCl_3$) δ 7.62–7.37 (m, 20H, 4Ph), 1.46 (t, $J = 13.2$, 6H, Me); ^{31}P NMR ($CDCl_3$) δ 44.5 (s); IR ν(CO) (CH_2Cl_2) 2019s, 1905s, 1881s cm^{-1}.

*Synthesis of [Mo(CO)$_4${Ph$_2$PCMe(Et)PPh$_2$}] (**11**).* To **3** (0.142 g, 0.2341 mmol) in thf (50 ml) was added MeLi (0.73 ml, 1.171 mmol) in diethyl ether. This caused the

solution to turn yellow-orange. After stirring for 1 h, EtI (0.093 ml, 1.171 mol) was added via syringe. There was little colour change upon its addition. The reaction mixture was allowed to stir for 3 days before removal of volatiles which gave a viscous yellow-orange oil. This was dissolved in dichloromethane (50 ml), washed with water (3 × 40 ml), dried over magnesium sulphate and filtered to give a clear yellow solution. This was concentrated on a rotary evaporator and the resulting solution was layered with methanol to yield **11** as yellow crystals (0.137 g, 92%). ^{1}H NMR ($CDCl_3$) δ 7.77–7.32 (m, 20H), 2.30 (m, 2H, Et), 1.15 (t, $J = 16.3$, 3H, Me), 0.94 (t, $J = 7.4$, 3H, Me); ^{31}P NMR ($CDCl_3$) δ 48.5 (s); IR ν(CO) (CH_2Cl_2) 2018s, 1903s, 1880s cm^{-1}. Anal. Calc. for **11**: C, 60.60, H, 4.45. Found: C, 60.02, H, 4.46%.

*Synthesis of [Mo(CO)$_4${Ph$_2$PCMe(Pr)PPh$_2$}] (**12**).* To **4** (0.31 g, 0.487 mmol) in thf (50 ml) was added MeLi (1.5 ml, 2.443 mmol) the solution turning dark brown. This was stirred for 1 h followed by addition of MeI (0.18 ml, 2.931 mmol). This caused the solution to turn dark brown-orange. After 3 days the solution was evaporated to give a viscous brown oil. This was dissolved in dichloromethane (50 ml), washed with water (3 × 40 ml) and the dichloromethane portion was dried over magnesium sulphate. After filtration and concentration under vacuum it was layered with methanol. As the solvents slowly mixed, crystals were obtained (0.25 g, 80%). ^{1}H NMR ($CDCl_3$) δ 7.54–7.33 (m, 20H, Ph), 2.16 (m, 2H, CH_2), 1.35 (m, 2H, CH_2), 0.86 (t, $J = 7.2$, 3H, Me), 1.18 (t, $J = 16.4$, 3H, Me);^{31}P NMR ($CDCl_3$) δ 48.9 (s); IR ν(CO) (CH_2Cl_2) 2018s, 1903s, 1880s cm^{-1}. Anal. Calc. for **12**: C, 58.21, H, 4.49. Found: C, 57.82, H, 5.02.

*Synthesis of [Mo(CO)$_4${Ph$_2$PCMe(Bu)PPh$_2$}] (**13**).* To **5** (0.33 g, 0.588 mmol) in thf (50 ml) was added MeLi in diethyl ether (1.59 ml, 2.54 mmol) causing the reaction mixture to turn dark brown. After 1 h, MeI (0.21 ml, 3.52 mmol) was added, the reaction mixture turning dark brown-orange. This was stirred for 3 days and volatiles removed to give a sticky dark brown-orange oil. This was dissolved in dichloromethane (50 ml) and washed with water (3 × 40 ml). The dichloromethane portion was dried over magnesium sulphate and filtered. Crystals were obtained upon layering a concentrated dichloromethane solution with methanol and allowing the two layers to mix very slowly. Further crystals were obtained upon slow evaporation of the solvent (0.23 g, 68%). ^{1}H NMR ($CDCl_3$) δ 7.55–7.32 (m, 20H, Ph), 1.45 (t, $J = 13.3$, 2H, CH_2), 1.25–1.08 (m, 2H, CH_2), 0.75 (t, $J = 7.2$, 3H, Me), 0.58 (t, $J = 3$H, Me); ^{31}P NMR ($CDCl_3$) δ 48.9 (s); IR ν(CO) (CH_2Cl_2) 2018s, 1903s, 1880s cm^{-1}. Anal. Calc. for **13**: C, 61.38, H, 4.87. Found: C, 60.48, H, 4.86%.

*Synthesis of [Mo(CO)$_4${Ph$_2$PCMe(allyl)PPh$_2$}] (**14**).* To **6** (0.41 g, 0.64 mmol) in thf (20 ml) was added MeLi (0.11 ml, 1.8 mmol) causing it to turn bright orange. This was stirred for 30 min and MeI (0.11 ml, 1.8 mmol) added causing the solution to turn orange-yellow. The mixture was stirred overnight and volatiles were removed to give an oily solid. This was dissolved in dichloromethane (20 ml) and washed with water (3 × 30 ml). The dichloromethane portion was then dried over magnesium sulphate, filtered and concentrated on a rotary evaporator. This solution was layered with methanol and the two solutions were allowed to mix slowly, yielding crystals (0.34 g, 82%). ^{1}H NMR ($CDCl_3$) δ 7.78–7.30 (m, 20H, Ph), 5.64 (m, 1H, CH), 5.08 (d, $J = 9.7$, 1H, CH_2), 4.79 (d, $J = 17.7$, 1H, CH_2), 3.01 (m, 2H, CH_2), 1.18 (t, $J = 16.0$, 3H, Me); ^{31}P NMR ($CDCl_3$) δ 49.3 (s); IR ν(CO) (CH_2Cl_2) 2019s, 1905s, 1881s cm^{-1}. Anal. Calc. for **14**: C, 61.31, H, 4.37. Found: C, 60.68, H, 4.35%.

*Synthesis of [Mo(CO)$_4${Ph$_2$PC(allyl)$_2$PPh$_2$}] (**15**).* To **6** (0.25 g, 0.39 mmol) in thf (20 ml) was added *t*-BuLi (0.23 ml, 0.39 mmol) to give an orange solution. This was stirred for 1 min and then allyl iodide (0.10 ml, 1.18 mmol) was added. The solution turned yellow and was stirred for 15 min. After removal of volatiles, NMR analysis revealed a poor conversion to the desired product. Hence, the oily solid was redissolved in dry thf, and *t*-BuLi (0.93 ml, 1.57 mmol) and allyl iodide (0.22 ml, 2.37 mmol) were again added. This procedure was carried out a further five times. At this stage removal of volatiles gave a viscous oil which was dissolved in dichloromethane (20 ml), washed with water (3 × 30 ml) and dried with magnesium sulphate. After filtration this gave a dry solid which was washed with a hexane (5 ml). This was redissolved in the minimum amount of dichloromethane and layered with methanol to give a yellow crystalline solid. ^{31}P NMR showed this to be a mixture of **6** and **15** (ca. 1:2). ^{1}H NMR ($CDCl_3$) δ 7.78–7.42 (m, 20H, Ph), 5.23 (qt, $J = 10.0$, 6.9, 2H, CH), 4.71 (dd, $J = 10.6$, 1.1, 2H, =CH_2), 4.42 (dd, $J = 17.0$, 1.4, 2H, =CH_2), 2.97 (dt, $J = 12.4$, $J = 6.7$, 4H, CH_2);^{31}P NMR ($CDCl_3$) δ 49.8 (s); IR ν(CO) (CH_2Cl_2) 2019s, 1904s, 1888s cm^{-1}.

*Synthesis of [W(CO)$_4${Ph$_2$PC(Me$_2$)PPh$_2$}] (**16**) [68].* To **7** (0.20 g, 0.32 mmol) in thf (35 ml) was added MeLi (0.99 ml, 1.6 mmol) giving rise to a colour change from yellow to bright yellow. This was allowed to stir for 15 min before adding MeI (0.12 ml, 1.9 mmol). Heat was evolved upon the addition of MeI and the solution turned orange. The reaction mixture was then left to stir for 2 h. The solvent was then removed under vacuum leaving a dry solid. Analysis of the solid by ^{31}P NMR spectroscopy showed that only a moderate conversion to **16** so the solid was redissolved in dry thf and the procedure repeated. The reaction mixture was then pumped down to a solid and dissolved in dichloromethane (ca. 20 ml). This solution was washed with aliquots of water (3 × 30 ml) and dried with anhydrous magnesium sulphate. The solution was filtered and concentrated on a rotary evaporator. Crystals were yielded by layering the dichloromethane solution with methanol and then leaving the mixture to allow the two solvents to mix slowly (0.20 g, 94%). ^{1}H NMR ($CDCl_3$) δ: 7.63–7.37 (m, 20H, Ph), 1.45 (t, $J = 13.6$, 6H, Me); ^{31}P NMR ($CDCl_3$) δ 21.2 (s, $J_{P-W} = 103.9$).

*Synthesis of [Mo(CO)$_4$(dcpm)] (**17**).* dcpm (0.170 g, 0.41 mmol) and *cis*-[Mo(CO)$_4$(NHC$_5$H$_{10}$)$_2$] (0.158 g, 0.41 mmol) were refluxed in dichloromethane (10 ml) for $2\frac{1}{2}$ h. The solution was cooled to room temperature before being filtered. Methanol (15 ml) was added and the mixture was placed in the freezer overnight yielding pale yellow crystals (0.15 g, 55%). ^{1}H NMR (CDCl$_3$) δ 2.87 (t, $J = 8.0$, 2H, CH$_2$), 1.91–1.25 (m, 44H, Cy); ^{31}P NMR (CDCl$_3$) δ 13.2 (s); IR ν(CO) (CH$_2$Cl$_2$) 2008s, 1891s, 1866s cm^{-1}. Anal. Calc. for **17**: C, 56.49, H, 7.52. Found: C, 54.34, P, 9.95%. Mass spectrum (FAB): *m*/*z* 616 (MH$^+$), 530 (M$^+$−2CO).

*Synthesis of [W(CO)$_4$(dcpm)] (**18**).* dcpm (0.175 g, 0.43 mmol) and *cis*-[W(CO)$_4$(NHC$_5$H$_{10}$)] (0.202 g, 0.43 mmol) were refluxed in dichloromethane (10 ml) for $4\frac{1}{2}$ h. After cooling, the reaction mixture was filtered and methanol (20 ml) was added. The dark orange solution was then put in the freezer. The crystals that formed were removed and the solution was concentrated on a rotary evaporator before being returned to the freezer to obtain a second batch (0.267 g, 90%). ^{1}H NMR (CDCl$_3$) δ 3.26 (t, $J = 8.33$, 2H, CH$_2$), 1.92–1.26 (m, 44H, Cy); ^{31}P NMR (CDCl$_3$) δ −10.6 (s, $J_{P-W} = 96.7$); IR ν(CO) (CH$_2$Cl$_2$) 2004s, 1880s, 1860s cm^{-1}. Anal. Calc. for **18**: C, 49.44, H, 6.58, P, 8.79. Found: C, 48.94, H, 6.62, P, 8.94%. Mass spectrum (FAB): *m*/*z* 704 (M$^+$), 616 (M$^+$−3CO), 409 (LH$^+$).

*Synthesis of [Mo(CO)$_4${Cy$_2$PCH(Me)PCy$_2$}] (**19**).* To **17** (0.180 g, 0.29 mmol) in thf (25 ml) was added *n*-BuLi (0.18 ml, 0.29 mmol) and this was stirred for 1 h. MeI (0.07 ml, 1.15 mmol) was then added to the dark yellow reaction mixture causing it to turn dark orange. After stirring overnight, volatiles were removed down to give an orange solid. This solid was dissolved in dichloromethane (20 ml), washed with water (3 × 30 ml), dried over magnesium sulphate and concentrated on a rotary evaporator. Methanol was then added and the mixture placed in a freezer overnight, yielding small orange crystals (0.164 g, 82%). These were isolated and washed with petrol before drying under vacuum. ^{1}H NMR (CDCl$_3$) δ 3.52 (m, 1H, CH), 2.17–1.27 (m, 47H, Cy and Me); ^{31}P NMR (CDCl$_3$) δ 32.7 (s); IR ν(CO) (CH$_2$Cl$_2$) 2006s, 1886s, 1866s cm^{-1}. Anal. Calc. for **19**: C, 57.01, H, 7.67. Found: C, 55.15, H, 7.54%.

*Synthesis of [Mo(CO)$_4${Cy$_2$PCH(Et)PCy$_2$}] (**20**).* To **17** (0.151 g, 0.244 mmol) in thf (50 ml) was added *n*-BuLi (0.2 ml, 0.32 mmol) turning the solution dark yellow. EtI (0.078 ml, 0.976 mmol) was added to give a dark orange-brown solution which was stirred overnight. Removal of volatiles gave an oily brown solid which was dissolved in dichloromethane (50 ml) and washed with water (3 × 25 ml). The dichloromethane portion was dried over magnesium sulphate, filtered and pumped down. Crystals were obtained by redissolving the solid in the minimum amount of dichloromethane and layering this with methanol (0.075 g, 48%). After mixing, slow evaporation yielded crystals suitable for X-ray diffraction. ^{1}H NMR (CDCl$_3$) δ 3.18 (m, 1H, CH), 1.89–1.25 (m, 46H, CH$_2$ and Cy), 0.98 (t, $J = 7.4$, 3H, Me);^{31}P NMR (CDCl$_3$) δ 36.6 (s); IR ν(CO) (CH$_2$Cl$_2$) 2007s, 1887s, 1867s cm^{-1}. Anal. Calc. for **20**: C, 57.76, H, 7.82. Found: C, 56.51, H, 7.64%. Mass spectrum (FAB): *m*/*z* 646 (M$^+$), 618 (M$^+$−CO).

*Synthesis of [Mo(CO)$_4${Cy$_2$PCH(allyl)PCy$_2$}] (**21**).* To **17** (0.19 g, 0.3 mmol) in thf (20 ml) was added *n*-BuLi (0.49 ml, 1.2 mmol) causing the solution to turn dark yellow. This was stirred for 1 min and allyl iodide (0.17 ml, 1.8 mmol) added, turning the mixture dark red. This was stirred for 15 min and volatiles were removed to give a dark solid. A^{31}P NMR spectrum revealed that there had not been full conversion so the solid was redissolved in thf and the procedure was repeated. After this, removal of volatiles gave an oily solid which was dissolved in dichloromethane (20 ml) and washed with water (3 × 30 ml). The dichloromethane solution was then dried over magnesium sulphate, filtered and volatiles removed to give a dry solid. Crystals were obtained by dissolving the solid in the minimum amount of dichloromethane and then layering the solution with methanol (0.19 g, 92%). ^{1}H NMR (CDCl$_3$)δ: 5.71 (m, 1H, CH), 5.06 (t, $J = 5.00$, $J = 11.0$, 2H, CH$_2$), 3.47 (m, 1H, CH), 2.53 (quin, $J = 8.09$, 2H, CH$_2$), 2.15–0.85 (m, 44H, Cy); ^{31}P NMR (CDCl$_3$) δ 37.1 (s); IR ν(CO) (CH$_2$Cl$_2$) 2008s, 1889s, 1868s cm^{-1}. Anal. Calc. for **21**: C, 58.53, H, 7.67. Found: C, 58.91, H, 8.25%.

X-ray data collection and solution. Single crystals were mounted on glass fibres and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 150 ± 2 K. Data reduction was carried out with SAINT+ [83] and absorption correction applied using the program SADABS [84]. Structures were generally solved by direct methods [85] and developed [86] using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically except for the two disordered molecules of methanol in **19** which were refined only isotropically. In **20** the methyl carbon of the backbone, C(6), was disordered over two sites (50:50). Hydrogens were generally placed in calculated positions (riding model) but in **19** the hydrogen atoms were not located or fixed on the methanol molecules, while hydrogen atoms were also omitted from the ethyl group in **20**. Structure solution used SHELXTL-PLUS V6.10 program package [87]. Full structural details are summarized in Table 2.

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Appendix A. Supplementary material

CCDC 658767, 658768, 658769, 658770, 658771, 658772, 658773, 658774 and 658775 contain the supple-

mentary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.09.024.

References

[1] R.J. Puddpehatt, Chem. Soc. Rev. (1983) 99.
[2] B. Chaudret, B. Delavaux, R. Poilblanc, Coord. Chem. Rev. 86 (1988) 134.
[3] G.K. Anderson, Adv. Organomet. Chem. 35 (1993) 1.
[4] S.J. Dossett, A. Gillon, A.G. Orpen, J.S. Fleming, P.G. Pringle, D.F. Wass, M.D. Jones, Chem. Commun. (2001) 699.
[5] N.A. Cooley, S.M. Green, D.F. Wass, K. Heslop, A.G. Orpen, P.G. Pringle, Organometallics 20 (2001) 4769.
[6] A. Carter, S.A. Cohen, N.A. Cooley, A. Murphy, J. Scutt, D.F. Wass, Chem. Commun. (2002) 858.
[7] J.N.L. Dennett, A.L. Gillon, K. Heslop, D.J. Hyett, J.S. Fleming, C.E. Lloyd-Jones, A.G. Orpen, P.G. Pringle, D.F. Wass, J.N. Scutt, R.H. Weatherhaed, Organometallics 26 (2004) 6077.
[8] L.E. Bowen, D.F. Wass, Organometallics 25 (2006) 555.
[9] D.F. Wass, Dalton Trans. (2007) 816.
[10] L.E. Bowen, M.F. Haddow, A.G. Orpen, D.F. Wass, Dalton Trans. (2007) 1160.
[11] T. Agapie, S.J. Schofer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 126 (2004) 1304.
[12] K. Blann, A. Bollmann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto, Chem. Commun. (2005) 620.
[13] M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, F. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto, Chem. Commun. (2005) 622.
[14] A. Bollmann, K. Blann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.S. McGuiness, D.H. Morgan, A. Neveling, S. Otto, M. Overett, A.M.Z. Slawin, P. Wasserscheid, S. Kuhlmann, J. Am. Chem. Soc. 126 (2004) 14712.
[15] G. Hoge, H.-P. Wu, W.S. Kissel, D.A. Pflum, D.J. Greene, J. Bao, J. Am. Chem. Soc. 126 (2004) 5966.
[16] H.-P. Wu, G. Hoge, Org. Lett. 6 (2004) 3645.
[17] S.M. Hansen, F. Rominger, M. Metz, P. Hofmann, Chem. Eur. J. 5 (1999) 557.
[18] P. Hofmann, C. Meier, W. Hiller, M. Heckel, J. Riede, M.U. Schmidt, J. Organomet. Chem. 490 (1995) 51.
[19] J.V. Barkley, M. Ellis, S.J. Higgins, M.K. McCart, Organometallics 17 (1998) 1725.
[20] J.V. Barkley, J.C. Grimshaw, S.J. Higgins, P.B. Hoare, M.K. McCart, A.K. Smith, J. Chem. Soc., Dalton Trans. (1995) 2901.
[21] N. Simhai, C.N. Iverson, B.L. Edelbach, W.D. Jones, Organometallics 20 (2001) 2759.
[22] C. Mueller, C.N. Iverson, R.J. Lachicotte, W.D. Jones, J. Am. Chem. Soc. 123 (2001) 9718.
[23] C.N. Iverson, W.D. Jones, Organometallics 20 (2001) 5745.
[24] C.N. Iverson, R.J. Lachicotte, C. Mueller, W.D. Jones, Organometallics 21 (2002) 5320.
[25] G. Ewart, A.P. Lane, J. McKechnie, D.S. Payne, J. Chem. Soc. A (1964) 1543.
[26] V.H. Noth, L. Meinel, Z. Anorg. Allg. Chem. 349 (1967) 225.
[27] D.F. Clemens, M.L. Caspar, D. Rosenthal, R. Peluso, Inorg. Chem. 9 (1970) 960.
[28] V.W. Seidel, M. Alexiev, Z. Anorg. Allg. Chem. 438 (1978) 4221.
[29] P. Bhattacharyya, J.D. Woollins, Polyhedron 14 (1995) 3367.
[30] R.P. Kamalesh Babu, S.S. Krishnamurthy, M. Nethaji, Tetrahedron: Asymmetry 6 (1995) 427.
[31] P. Braunstein, H.-P. Kormann, W. Meyer-Zaika, R. Pugin, G. Schmid, Chem. Eur. J. 6 (2000) 4637.
[32] E.J. Sekabunga, M.L. Smith, T.R. Webb, W.E. Hill, Inorg. Chem. 41 (2002) 1205.
[33] Z. Fei, R. Scopelliti, P.J. Dyson, Dalton Trans. (2003) 2772.
[34] M.S. Balakrishna, T.K. Prakasha, S.S. Krishnanmurthy, U. Siriwardane, N.S. Hosmane, J. Organomet. Chem. 390 (1990) 203.
[35] Z.Z. Zhang, A. Yu, H.P. Xi, R.J. Wang, H.G. Wang, J. Organomet. Chem. 470 (1994) 223.
[36] J. Ellermann, L. Mader, Spectrochim. Acta A 37 (1981) 449.
[37] A.M.Z. Slawin, H.L. Milton, J. Wheatley, J.D. Woollins, Polyhedron 23 (2004) 3125.
[38] V. Gato, P. Mastrorilli, C.F. Noble, P. Braunstein, U. Englert, Dalton Trans. (2006) 2342.
[39] K.G. Gaw, M.B. Smith, J.W. Steed, J. Organomet. Chem. 664 (2002) 294.
[40] Z. Weng, S. Teo, T.S.A. Hor, Dalton Trans. (2007) 3493.
[41] K. Issleib, D.W. Muller, Chem. Ber. 92 (1959) 3175.
[42] M.T. Honaker, B.J. Sandefur, J.L. Hargett, A.L. McDaniel, R.N. Salvatore, Tetrahedron Lett. 44 (2003) 8373.
[43] F. Eisentraeger, A. Goethlich, I. Gruber, H. Heiss, C.A. Kiener, C. Krueger, J.U. Notheis, F. Rominger, G. Scherhag, M. Schultz, B.F. Straub, M.A.O. Volland, P. Hofmann, New J. Chem. 27 (2003) 540.
[44] J. Wolf, M. Manger, U. Schmidt, G. Fries, D. Barth, B. Weberndörfer, D.A. Vicic, W.D. Jones, H. Werner, Dalton Trans. (1999) 1867.
[45] Z.S. Novikova, A.A. Prishchenko, I.F. Lutsenko, Zh. Obshch. Khim. 47 (1977) 755.
[46] F.L. Joslin, J.T. Mague, D.M. Roundhill, Polyhedron 10 (1991) 1713.
[47] S.O. Grim, J.D. Mitchell, Inorg. Chem. 16 (1977) 1770.
[48] S.O. Grim, P.H. Smith, I.J. Colquhoun, W. McFarlane, Inorg. Chem. 19 (1980) 3195.
[49] R. Appel, K. Geisler, H.-F. Schöler, Chem. Ber 112 (1979) 648.
[50] J.S. Yu, I.P. Rothwell, J. Chem. Soc., Chem. Commun. (1992) 632.
[51] M. Filby, A.J. Deeming, G. Hogarth, M.-Y. Lee, Can. J. Chem. 84 (2006) 319.
[52] P.W. Clark, B.J. Mulraney, J. Organomet. Chem. 217 (1981) 51.
[53] N.D. Jones, P. Meessen, M.B. Smith, U. Losehand, S.J. Rettig, B.O. Patrick, B.R. James, Can. J. Chem. 80 (2002) 1600.
[54] A.A. Prishchenko, N.E. Nifant'ev, Z.S. Novikova, I.F. Lutsenko, Zh. Obs. Khim. 50 (1980) 1881.
[55] N.M. Doherty, G. Hogarth, S.A.R. Knox, K.A. Macpherson, F. Melchior, D.A.V. Morton, A.G. Orpen, Inorg. Chim. Acta 198–200 (1992) 257.
[56] L. Hao, I.R. Jobe, J.J. Vittal, R.J. Puddephatt, Organometallics 14 (1995) 2781.
[57] J. Campora, C. Maya, I. Mates, B. Claasen, P. Palma, E. Alvarez, Inorg. Chim. Acta 359 (2006) 3191.
[58] W. Hewertson, N.R. Watson, J. Chem. Soc. (1962) 1490.
[59] C.-L. Lee, Y.-P. Yang, S.J. Rettig, B.R. James, D.A. Nelson, M.A. Lilga, Organometallics 5 (1986) 2220.
[60] C.S. Kraihanzel, P.K. Maples, J. Organomet. Chem. 117 (1976) 159.
[61] L.J. Al-Hayaly, Transition Met. Chem. 23 (1998) 221.
[62] A. Pons, O. Rossell, M. Seco, X. Solans, M. Font-Bardía, J. Organomet. Chem. 514 (1996) 177.
[63] H. Schmidbaur, T. Pollock, Helv. Chim. Acta 67 (1984) 2175.
[64] L. Braun, P. Liptau, G. Kehr, J. Ugolotti, R. Froehlich, G. Erker, Dalton Trans. (2007) 1409.
[65] G.F. Meijs, J. Org. Chem. 52 (1987) 3923.
[66] S. Al-Jibori, B.L. Shaw, J. Chem. Soc., Chem. Commun. (1982) 286.
[67] S. Al-Jibori, B.L. Shaw, Inorg. Chim. Acta 65 (1982) L123.
[68] S. Al-Jibori, B.L. Shaw, Inorg. Chim. Acta 74 (1983) 235.
[69] S. Al-Jibori, M. Hall, A.T. Hutton, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1984) 863.
[70] S. Al-Jibori, B.L. Shaw, J. Organomet. Chem. 273 (1984) 213.
[71] G.R. Copper, D.M. McEwan, B.L. Shaw, Inorg. Chim. Acta 122 (1986) 207.

[72] J.M. Vila, M. Lopez-Torres, C. Rodriguez, A.A. Fernadez, R. Mosteiro, J.J. Fernandez, Trends Organomet. Chem. 4 (2002) 99.
[73] T.F. Lai, K.K. Cheung, K.S. Mok, J. Chem. Soc. A (1971) 1644.
[74] P.N. Riley, J.R. Clark, P.E. Fanwick, I.P. Rothwell, Inorg. Chim. Acta 288 (1999) 35.
[75] C.E. Kriley, C.J. Woolley, M.K. Krepps, E.M. Popa, P.E. Fanwick, I.P. Rothwell, Inorg. Chim. Aca 300–302 (2000) 300.
[76] C.E. Kriley, M.M. Majireck, J.M. Tobolewski, L.E. Kelvington, S.H. Cummings, S.J. Hershberger, J.D. Link, A.L. Silverio, P.E. Fanwick, I.P. Rothwell, Inorg. Chim. Acta 358 (2005) 57.
[77] H. Werner, G. Fries, B. Webendörfer, J. Organomet. Chem. 607 (2000) 182.
[78] J.K. Bera, P.E. Fanwick, R.A. Walton, Inorg. Chim Acta 311 (2000) 138.
[79] L. Jai, W. Fu, M. Yu, J. Zhang, Y. Chen, Acta Crystallogr., Sect. E 61 (2005) m858.
[80] F.I. Adam, G. Hogarth, I. Richards, J. Organomet. Chem. 692 (2007) 3957.
[81] M. Ardon, G. Hogarth, D.T.W. Oscroft, J. Organomet. Chem. 689 (2004) 2429.
[82] G. Hogarth, M. Ardon, P.D. Hayes, J. Chem. Educ. 79 (2002) 1249.
[83] Area detector control and data integration and reduction software, Brüker AXS, Madison, WI, 2001.
[84] SADABS, University of Göttingen: Göttingen, Germany, 1997.
[85] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
[86] G.M. Sheldrick, SHELXL: Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1993.
[87] SHELXTL-PLUS, Bruker AXS Inc., Madison, WI, 2001.