Small bite-angle diphosphines — Synthesis and structure of low-valent complexes of bis(di-*ortho*-tolylphosphino)methane (dotpm) and related ligands[1]

Maria Filby, Antony J. Deeming, Graeme Hogarth, and Mo-yin (Venus) Lee

Abstract: The coordination chemistry of bis(di-*ortho*-tolylphosphino)methane (dotpm) has been studied. It is an excellent chelating ligand and a range of low-valent mononuclear complexes have been prepared; *cis*-[$M(CO)_4(\eta^2$-dotpm)] (M = Cr, Mo, W; **1**–**3**), [$CpRuCl(\eta^2$-dotpm)] (**4**), and *cis*-[$MX_2(\eta^2$-dotpm)] (M = Pt, X = Cl, Br, I; **5a**–**5c**, M = Pd, X = Cl; **6**). The backbone protons are relatively acidic and can be deprotonated using *n*-BuLi or $LiN(SiMe_3)_2$. Subsequent alkylation by RX (X = halogen; R = Me, Et, CH_2Ph) affords *cis*-[$M(CO)_4(\eta^2$-Rdotpm)] (M = Cr, Mo, W, R = Me; **7**–**9**, M = Mo, W, R = Et, CH_2Ph; **12**–**15**), [$CpRuCl(\eta^2$-Medotpm)] (**10**), and *cis*-[$PtI_2(\eta^2$-Medotpm)] (**11**). Thermolysis of *cis*-[$Mo(CO)_4(\eta^2$-Medotpm)] (**8**) yields what is believed to be the coordinately and electronically unsaturated complex [$Mo(CO)_3(\eta^2$-Medotpm)] (**16**), suggesting that derivatives of dotpm (cone angle 194°) are bulky enough to stabilize a 16-electron complex. Crystal structures of **2**, **3**, **7**–**9**, **13**, and **14** have been determined (diphosphine bite angles ranging from 66.58(3)° to 70.96(5)°.

Key words: diphosphine, transition metal, bulky, carbonyl, *ortho*-tolyl.

Résumé : On a étudié la chimie de coordination du bis(di-*ortho*-tolylphosphino)méthane (dotpm). C'est un excellent ligand chélatant et on en a préparé un large éventail de complexes mononucléaires de faible valence, dont les *cis*-[$M(CO)_4(\eta^2$-dotpm)] (M = Cr, Mo, W; **1**–**3**), [$CpRuCl(\eta^2$-dotpm)] (**4**) et *cis*-[$MX_2(\eta^2$-dotpm)] (M = Pt, X = Cl, Br, I; **5a**–**5c**, M = Pd, X = Cl; **6**). Les protons du squelette sont relativement acides et peuvent être déprotonés en utilisant du *n*-BuLi ou du $LiN(SiMe_3)_2$. Des alkylations subséquentes par du RX (X = halogène; R = Me, Et, CH_2Ph) conduisent à la formation des *cis*-[$M(CO)_4(\eta^2$-Rdotpm)] (M = Cr, Mo, W, R = Me; **7**–**9**, M = Mo, W, R = Et, CH_2Ph; **12**–**15**), [$CpRuCl(\eta^2$-Medotpm)] (**10**) et *cis*-[$PtI_2(\eta^2$-Medotpm)] (**11**). La thermolyse du *cis*-[$Mo(CO)_4(\eta^2$-Medotpm)] (**8**) conduit à la formation d'un composé qu'on croit être le complexe coordonné et électroniquement insaturé [$Mo(CO)_3(\eta^2$-Medotpm)] (**16**) qui suggère que les dérivés dotpm (angle du cône de 194°) sont suffisamment encombrants pour stabiliser un complexe à 16 électrons. On a déterminé les structures cristallines des composés **2**, **3**, **7**–**9**, **13** et **14** dans lesquels l'angle de morsure de la diphosphine varie de 66,58(3)° à 70,96(5)°.

Mots clés : diphosphine, métal de transition, encombrant, carbonyle, *ortho*-tolyle.

[Traduit par la Rédaction]

Introduction

Diphosphines are an important subclass of tertiary phosphines that find widespread use in homogeneous catalysis. A key to their success in this area is the ability to tune their spatial demands by variation of substituents at phosphorus and also the nature of the adjoining backbone (1). When metal bound, they can chelate to a single metal atom or act as a bridge between two, thus forming a binuclear complex. In general, the optimum ring size for a diphosphine ligand is five, and while bis(diphenylphosphino)ethane (dppe) is an excellent chelating ligand, in contrast bis(diphenylphosphino)methane (dppm) behaves predominantly as a bridging ligand since chelatation results in the formation of a highly strained four-membered ring (2, 3). Small changes to dppm can, however, lead to marked changes in its coordination chemistry. For example, substitution of both backbone hydrogens for methyl groups, as in 2,2-bis(diphenylphosphino)propane (2,2-dppp), results in a pronounced change in behavior. While dppm acts as a bridg-

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Dedicated to Professor Arthur J. Carty in recognition of his unwavering enthusiasm for chemistry and unselfish dedication to the scientific community.

M. Filby, A.J. Deeming, G. Hogarth,[2] and M.-Y. Lee. Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK.

[1]This article is part of a Special Issue dedicated to Professor Arthur Carty.
[2]Corresponding author (e-mail: g.hogarth@ucl.ac.uk).

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ing ligand in the binuclear complex $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ (4), 2,2-dppp in contrast, forms exclusively, and in high yields, the chelate complex $[Fe(CO)_3(\eta^2\text{-}2,2\text{-}dppp)]$ (5).

While the chemistry of diphosphines with two or more backbone atoms has been extensively studied, the effect of varying the steric and electronic properties of dppm and related ligands are far more limited (6–10). Such properties can be fine-tuned in a systematic way by varying both backbone and nonbackbone substituents. In general greater steric crowding at the backbone will lead to a reduction in the bite angle and thus a stronger tendency to chelate. Recently, a number of important developments have been made in this area of small bite-angle diphosphines. Hoge et al. (11) at Pfizer have shown that $[Rh(t\text{-}Bu_2PCH_2P\text{-}t\text{-}BuMe)(COD)]^+$ exhibits superior enantioselectivity with lower catalyst loading than conventional asymmetric catalysts in asymmetric hydrogenation reactions, while Pringle and co-workers (12) have shown that nickel(II) complexes of $Ar_2PN(Me)NAr_2$ (Ar = Ph, *o*-tolyl, *o*-*i*-PrC_6H_4) are very efficient ethylene polymerization catalysts, giving high-molecular-weight linear polymer. Further, while the work described herein was in progress, Pringle's group also showed that nickel complexes with small bite-angle diphosphines based on a methylene backbone were also active towards ethylene polymerization, but produced highly branched low-molecular-weight polymer (13). This report prompted us to describe our work in the area of small bite-angle diphosphines. In this contribution we describe the synthesis of a number of low-valent bis(di-*ortho*-tolylphosphino)methane (dotpm) transition metal complexes together with related backbone substituted (Rdotpm) species. We have used VT NMR spectroscopy and X-ray crystallography to probe the effect of the changes in substituents on the bite angle and conformational preference of the metal-bound ligand.

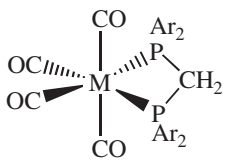
Results and discussion

Synthesis and characterization

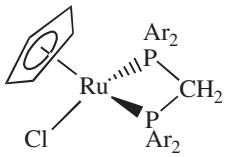
Bis(di-*ortho*-tolylphosphino)methane (dotpm) has previously been prepared by Clark and Mulraney (14) upon lithiation of di-*ortho*-tolylphosphinous chloride. We also prepared dotpm via this route, but found the lithiation of commercially available tri-*ortho*-tolylphosphine to be preferable. This method gave higher yields and proved easier to carry out mainly because of the ease of weighing out the tertiary phosphine. In contrast, di-*ortho*-tolylphosphinous chloride as we prepared it was very sticky and proved difficult to fully purify and handle. Dotpm is a white crystalline solid that can be stored indefinitely in air at room temperature. Characterization was straightforward and as found for dppm, the equivalent methylene protons couple only weakly to the phosphorus atoms ($J_{P\text{-}H}$ = 2.5 Hz).

Addition of dotpm to $[NEt_4][Cr(CO)_5]$ or *cis*-$[M(CO)_4(pip)_2]$ (pip = piperidine) afforded the expected tetracarbonyl complexes *cis*-$[M(CO)_4(\eta^2\text{-}dotpm)]$ (M = Cr, Mo, W) (**1**–**3**) in good yields (15). Likewise, thermolysis with $[CpRuCl(PPh_3)_2]$ at 110 °C gave $[CpRuCl(\eta^2\text{-}dotpm)]$ (**4**) in 76% yield after chromatography. Heating dotpm and $[MCl_2(PhCN)_2]$ (M = Pt, Pd) in dry dichloromethane cleanly afforded *cis*-$[PtCl_2(\eta^2\text{-}dotpm)]$ (**5a**) and *cis*-$[PdCl_2(\eta^2\text{-}dotpm)]$ (**6**), while the former was rapidly converted into the analogous dibromide, *cis*-$[PtBr_2(\eta^2\text{-}dotpm)]$ (**5b**), and diiodide, *cis*-$[PtI_2(\eta^2\text{-}dotpm)]$ (**5c**) upon addition of excess NaBr and NaI, respectively.

Characterization was relatively straightforward, key spectroscopic features being the downfield shift observed in the ^{31}P NMR spectrum upon coordination and the increase in the phosphorus-proton coupling constant to the methylene protons ($J_{P\text{-}H}$ = 7.9, 10.2 Hz). In all compounds (except **4**) the methylene protons are equivalent, being observed as a triplet in the ^1H NMR spectrum as expected for approximate C_{2v} symmetry. In **4** (C_s symmetry), the methylene protons are inequivalent being observed as two multiplets at δ 4.94 and 4.54 at 308 K. The different symmetries are also apparent in the tolyl resonances, with all exhibiting a single methyl resonance, except **4** where two methyl resonances are observed at room temperature.



1 M = Cr
2 M = Mo
3 M = W



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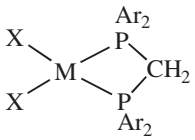
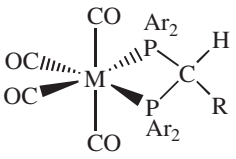


5a M = Pt, X = Cl
5b M = Pt, X = Br
5c M = Pt, X = I
6 M = Pd, X = Cl

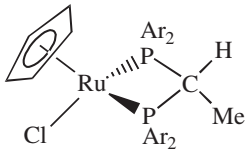
All proton NMR spectra show a temperature dependency with most being at the high temperature limit at room temperature or just above. We attribute these changes to the restricted rotation of the aryl groups about the phosphorus–carbon bonds. Variable-temperature ^1H NMR measurements were made for a number of examples; data for **4** being most useful. At 308 K, two sharp equal intensity singlets at δ 2.08 and 2.05 are assigned to the methyl substituents on the aryl rings. The aromatic region is complex at this temperature with some sharp and some broad signals, but each individual component (when identifiable) integrated to two protons. Clear signals at the low field (δ 8.08) and high field (δ 6.73) of this region integrated to two protons. Upon cooling, significant broadening of most of the spectrum is noted to 268 K, below which the peaks begin to sharpen again. At 228 K, three methyl signals are observed at δ 2.21, 2.13, and 1.87 in the ratio 1:1:2 — although application of a Gaussian function to the high-field signal shows that it consists of two closely spaced resonances. Further, the low-field aromatic resonance seen at δ 8.08 at 308 K splits into two equal intensity signals at δ 8.51 and 7.57 at 228 K, while the high-field aromatic signal at δ 6.73 splits into two resonances at δ 6.43 and 6.36. These changes are interpreted in terms of the freezing out of the restricted rotation of the *ortho*-tolyl

groups about the carbon–phosphorus bonds and taking the coalescence temperature for the δ 8.08 as 268 K, a rotational barrier of 50.6 (±1) kJ mol^{-1} can be estimated.

Shaw and co-workers (16–19) have previously shown that when dppm is coordinated to low-valent metal centres the backbone protons become relatively acidic. This is useful since it allows facile backbone functionalization. We have utilized this to prepare a number of backbone-substituted derivatives of dotpm (denoted Rdotpm). For example, backbone deprotonation of **1**–**3** using *n*-BuLi followed by a quench with methyliodide afforded the Medotpm complexes *cis*-[M(CO)$_4$(η^2-Medotpm)] (M = Cr, Mo, W) (**7**–**9**) in good yields, while [CpRuCl(η^2-Medotpm)] (**10**) was prepared similarly from **4** using LiN(SiMe$_3$)$_2$ as a base. Deprotonation of *cis*-[PtCl$_2$(η^2-dotpm)] (**5a**) by LiN(SiMe$_3$)$_2$ followed by addition of methyliodide afforded *cis*-[PtI$_2$(η^2-Medotpm)] (**11**), whereby the halides had also exchanged, while quenching the deprotonated molybdenum and tungsten complexes with ethyliodide or benzylbromide gave *cis*-[M(CO)$_4$(η^2-Etdotpm)] (M = Mo, W) (**12** and **13**) and *cis*-[M(CO)$_4$(η^2-Bzdotpm)] (M = Mo, W) (**14** and **15**), respectively.



7 M = Cr, R = Me
8 M = Mo, R = Me
9 M = W, R = Me
12 M = Mo, R = Et
13 M = W, R = Et
14 M = Mo, R = Bz
15 M = W, R = Bz



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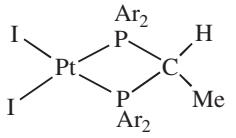

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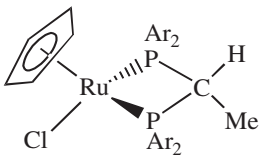
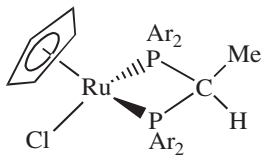
Characterization was again relatively straightforward. For all complexes, the remaining backbone proton was observed as a multiplet resonance being shifted slightly downfield of the analogous signal in dotpm complexes. The introduction of the substituent changes the symmetry of the complexes, such that those previously with C_{2v} symmetry are now in the C_s point group. This results in two sets of *ortho*-tolyl groups; those lying towards the substituent and those pointing away from it, which is reflected in the observation of two distinct methyl resonances in the ^{1}H NMR spectra. We have analyzed the spectrum of *cis*-[Mo(CO)$_4$(η^2-Bzdotpm)] (**14**) in some detail and this has allowed assignment of the benzyl and individual aryl protons (see the Experimental section). The methyl resonance at δ 2.15 is assigned to the aryl groups (Ar$_A$) that lie on the same side of the diphosphine as the benzyl group, while that at δ 1.82 is assigned to the *ortho*-tolyl groups that lie proximal to the remaining backbone proton. All ^{1}H NMR spectra are temperature dependent, which is again attributed to the restricted rotation of the aryl groups. For example, cooling **14** leads to a significant broadening of all peaks in the spectrum except those associated with the benzyl substituent. However, even at 213 K splitting into individual proton signals was not yet observed.

For [CpRuCl(η^2-Medotpm)] (**10**) two possible isomers are possible, with the methyl group pointing towards the chloride (**10a**) or the cyclopentadienyl group (**10b**). The ^{1}H NMR spectrum at room temperature is both complex and broad, making full assignment impossible. However, some regions are quite clear, most notably two sharp singlet resonances at δ 5.21 and 5.15 in an approximate 1:3 ratio being assigned to the cyclopentadienyl protons. This suggests that both isomers are formed and on the basis of adverse steric interactions we suggest that the major isomer is **10a** in which the methyl group points towards the chloride. The tolyl methyl substituents are broad at room temperature and only those assigned to the major isomer can be clearly distinguished, appearing as two broad singlets at δ 2.60 and 2.56. Upon cooling a number of changes occur. Most significantly at 278 K, the δ 2.56 signal splits into two new singlets at δ 2.70 and 2.51, while the δ 2.60 signal broadens significantly. By 258 K, four sharp singlets are seen at δ 2.96, 2.70, 2.50, and 2.22. With coalescence temperatures as 288 and 268 K, respectively, free energies of activation of 54.4 and 53.4 kJ mol^{-1} are calculated, suggesting that a single process with an activation energy of ca. 54 2 kJ mol^{-1} is responsible for the observed changes. This value is similar to that of 50.6 1 kJ mol^{-1} estimated for **4**, the higher barrier in **10a** relating to the greater steric hindrance. At 258 K, two further broad resonances can be seen at δ 2.79 and 2.34, which we assign to the methyl groups in **10b**.



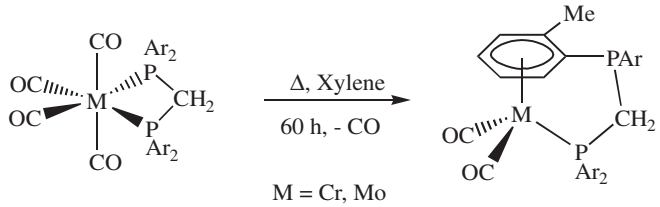
10a



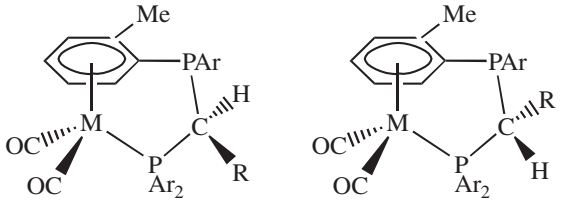
10b

All attempts to replace a second backbone proton were unsuccessful. This is probably a result of the decreasing acidity of the remaining proton upon addition of an electron-releasing substituent and also the decreased kinetic acidity resulting from the increased steric crowding. We did, however, obtain some evidence for a partial deprotonation of [Cr(CO)$_4$(η^2-Medotpm)] (**7**). Addition of an excess of *n*-BuLi followed by a quench with D$_2$O lead to a ^{1}H NMR spectrum in which the backbone proton signal integrated to ca. 60% of that expected for full occupancy.

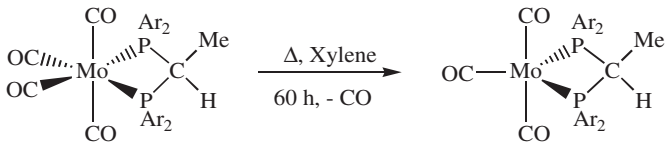
Complexes **1**–**3** have previously been prepared by Clark and Clark (15). The chromium and molybdenum complexes are reported to slowly lose CO upon heating in decalin to afford novel π-arene complexes.



We were interested in trying to make similar complexes with substituents on the backbone since such species would contain two chiral centres, and we envisaged that high diastereomeric control may occur because of the differing steric interactions between the methyl substituent on the bound arene ring and the backbone substituent.



Heating a toluene solution of **8** for 3 days resulted in no discernable change, however, heating a xylene solution of **8** for 2.5 days resulted in the formation of a dark solid, which we tentatively propose to be the 16-electon complex, $[Mo(CO)_3(\eta^2\text{-Medotpm})]$ (**16**). Characterization was based primarily on the observation of a singlet in the ^{31}P NMR spectrum, an M–CO ion in the +ve FAB mass spectrum, and two absorptions in the carbonyl region of the IR spectrum, the latter being indicative of a tricarbonyl arrangement. Similar properties have been observed for the related 16-electron complex, $[W(CO)_3(P\text{-}i\text{-}Pr_3)_2]$, which is black, poorly soluble in hexane, and shows a singlet in the ^{31}P NMR spectrum (20). In contrast to **16**, however, $[W(CO)_3(P\text{-}i\text{-}Pr_3)_2]$ and related 16-electron tricarbonyl complexes exhibit three carbonyl bands in the IR spectrum. This difference may be due to the differing symmetry at the metal centre. For example, the crystal structure of $[W(CO)_3(P\text{-}i\text{-}Pr_3)_2]$ shows that the P-W-P angle is 160.94(4)° (i.e., approximately trans), while in **16** it is likely to be nearer 66° to 67° observed in the crystallographically characterized molybdenum complexes described in the following section. Unfortunately, owing to the air-sensitive nature of **16** we have not been able to obtain a satisfactory elemental analysis.



8 **16**

While **16** is the major product of the prolonged heating of **8**, close scrutiny of the crude ^1H NMR spectrum of the reaction mixture reveals the formation of a small amount (<10%) of a second species presumed to be the expected π-bound arene complex. A series of unresolved signals between δ 5.5–4.5 is indicative of a π-bound arene, and there are a series of sharp singlets in the methyl region of the spectrum. While it is not possible to fully discern the nature of this species, there appears to be eight resonances between δ 5.5–4.5 falling into two sets in an approximate 2:1 ratio, suggesting that both diastereoisomers are formed.

Structural studies

To gain more insight into the precise structural features of dotpm and Rdotpm ligands we have carried out crystallographic studies on isostructural *cis*-$[M(CO)_4(\eta^2\text{-dotpm})]$ (M = Mo, W) (**2**, **3**), isostructural *cis*-$[M(CO)_4(\eta^2\text{-Medotpm})]$ (M = Cr, Mo, W) (**7**–**9**), *cis*-$[W(CO)_4(\eta^2\text{-Etdotpm})]$ (**13**), and *cis*-$[Mo(CO)_4(\eta^2\text{-Bzdotpm})]$ (**14**). The results of these are summarized in Figs. 1–4 and Tables 1 and 2. In all, the diphosphine subtends a small bite angle, ranging between 66.58(3)° and 70.96(5)°, with molybdenum and tungsten complexes being at the bottom end, and chromium and ruthenium compounds at the top end of the range. The best comparison of dppm and dotpm complexes is that between **2** and *cis*-$[Mo(CO)_4(\eta^2\text{-dppm})]$ (21); bite angles of 67.20(3)° and 67.3(1)°, respectively, being essentially the same, as are most of the other structural parameters except the P-C-P angle, which at 99.9(2)° in **2** is significantly greater than that of 95.6(4)° in *cis*-$[Mo(CO)_4(\eta^2\text{-dppm})]$. This results from a slight elongation (0.037 avg.) of the molybdenum–phosphorus bonds in **2** vs. those in the dppm complex, probably resulting from the greater steric demands of the *ortho*-tolyl vs. phenyl substituents. Introduction of a methyl or ethyl substituent on the backbone leads to a slight increase in the bite angle and a more significant reduction in the P-C-P an-

Fig. 1. Molecular structure of *cis*-$[Mo(CO)_4(\eta^2\text{-dotpm})]$ (**2**).

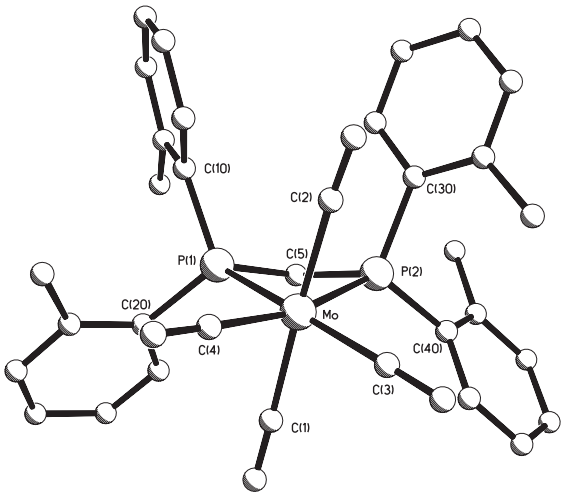


Fig. 2. Molecular sturcture of *cis*-$[Mo(CO)_4(\eta^2\text{-Medotpm})]$ (**7**).

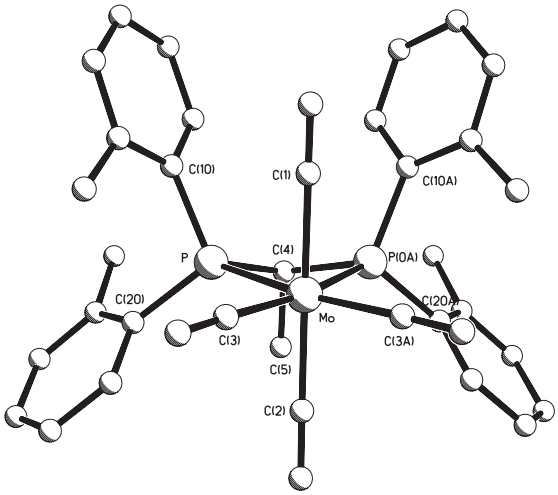


Table 1. Selected bond lengths (Å) and angles (°) for dtopm and Rdotpm complexes and related compounds.

Compound	M—CO (cis) (Å)	M—CO (trans) (Å)	M—P (Å)	P-M-P (°)	P-C-P (°)
cis-[Mo(CO)$_4$(η^2-dotpm)] (**2**)	2.028(5), 2.051(5)	1.979(4), 1.981(5)	2.5338(11), 2.5561(10)	67.20(3)	99.2(2)
cis-[W(CO)$_4$(η^2-dotpm)] (**3**)	2.039(11), 2.046(11)	1.980(10), 1.989(11)	2.524(2), 2.545(2)	67.00(7)	98.2(4)
cis-[Cr(CO)$_4$(η^2-Medotpm)] (**7**)	1.873(7), 1.903(7)	1.847(5)	2.3995(12)	70.96(5)	95.5(2)
cis-[Mo(CO)$_4$(η^2-Medotpm)] (**8**)	1.993(8), 2.042(8)	1.972(5)	2.5502(12)	67.66(5)	97.6(3)
cis-[W(CO)$_4$(η^2-Medotpm)] (**9**)	2.012(14), 1.979(14)	1.978(10)	2.527(2)	67.68(8)	96.6(4)
cis-[W(CO)$_4$(η^2-Etdotpm)] (**13**)	2.00(2), 2.03(2)	2.00(2), 2.00(2)	2.522(4), 2.536(4)	67.65(13)	95.7(6)
cis-[Mo(CO)$_4$(η^2-Bzdotpm)] (**14**)	2.021(3), 2.031(4)	1.963(4), 1.990(3)	2.5378(8), 2.5767(9)	66.58(3)	96.33(13)
cis-[Mo(CO)$_4$(η^2-dppm)][a]	2.07(1), 2.02(2)	1.92(1), 1.94(1)	2.501(2), 2.535(3)	67.3(1)	95.6(4)
mer-[Cr(CO)$_3$(η^2-dppm)(η^1-dppm)][b]	1.87(1), 1.86(1)	1.80(1)	2.298(4), 2.395(4)	71.1(1)	94.0(5)
fac-[W(CO)$_3$(MeCN)(η^2-dppm)][c]	1.929(6)	1.962(6), 1.970(8)	2.512(2), 2.514(2)	67.5(1)	98.1(3)
[PtCl$_2$(η^2-Ar$_2$PCH$_2$PAr$_2$)] (Ar = *o*-*i*-PrC$_6$H$_4$)[d]			2.2202(9), 2.2301(9)	75.96(3)	—

[a]Reference 21.
[b]Reference 22.
[c]Reference 23.
[d]Reference 13.

Fig. 3. Molecular structure of *cis*-[W(CO)$_4$(η^2-Edotpm)] (**13**).

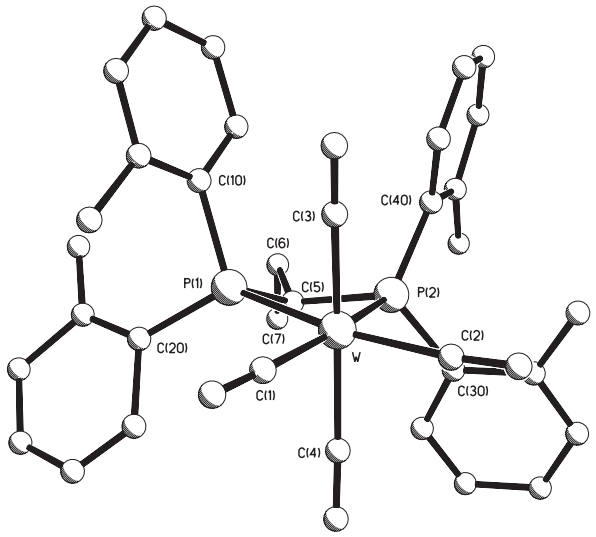
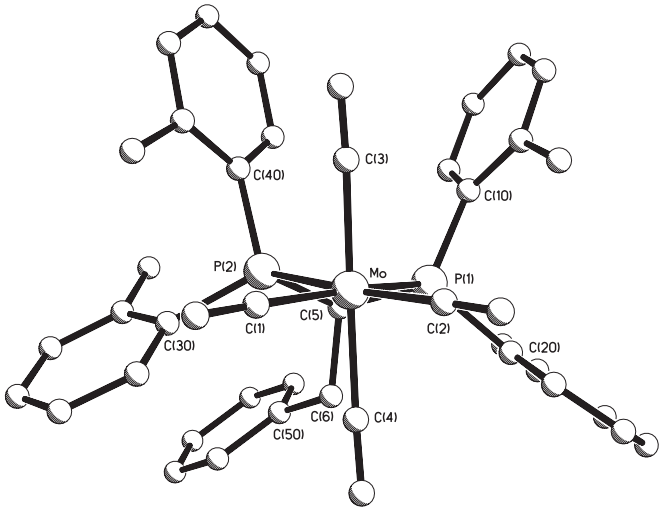


Fig. 4. Molecular structure of *cis*-[Mo(CO)$_4$(η^2-Bzdotpm)] (**14**).



gle of ca. 2°, while introduction of the bulky benzyl group leads to the smallest bite angle of 66.58(3)° observed in **14**.

In all the structures, the two *ortho*-tolyl groups on each phosphorus atom adopt a staggered-type arrangement, whereby the methyl groups are orientated in opposite directions, presumably to minimize adverse steric interactions. Further, for complexes carrying a backbone substituent, as expected, the *ortho*-tolyl groups lying on the same side as the substituent point away from it and thus the presence of the substituent dictates the orientational preference of the diphosphine ligand. The benzyl substituent in *cis*-[Mo(CO)$_4$-(η^2-Bzdotpm)] (**14**) is orientated such that there is a relatively close contact with one on the tolyl ligands, indicative of a π-stacking-type interaction. The structural arrangement adopted renders all the *ortho*-tolyl groups inequivalent. The appearance of two sets of aryl resonances at room temperature in solution shows that rotation of the benzyl group must be facile at this temperature and it may well be associated with a geared rotation of the *ortho*-tolyl groups.

Table 2. Crystallographic data for new compounds.

Compound	**2**	**3**	**7**	**8**	**9**	**13**	**14**
Chemical formula	$MoP_2O_4C_{34}H_{32}Cl$	$WP_2O_4C_{34}H_{32}Cl$	$CrP_2O_4C_{35}H_{34}Cl_2$	$MoP_2O_4C_{35}H_{34}Cl_2$	$WP_2O_4C_{35}H_{34}Cl_2$	$WP_2O_4C_{35}H_{34}$	$MoP_2O_4C_{40}H_{36}$
MW	697.93	785.84	03.46	747.40	835.31	764.41	738.57
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/m$	$P2_1/m$	$P2_1/m$	*Pbca*	$P2_1/c$
a (Å)	11.522(2)	11.526(2)	8.604(2)	8.639(2)	8.604(2)	17.167(3)	11.778(2)
b (Å)	18.292(4)	18.230(4)	19.750(4)	19.797(4)	19.708(4)	17.596(4)	15.230(3)
c (Å)	15.739(3)	15.717(3)	10.338(2)	10.501(2)	10.424(2)	21.436(4)	20.307(4)
α (°)	90	90	90	90	90	90	90
β (°)	99.45(3)	99.59(3)	92.37(3)	92.26(3)	92.44(3)	90	104.87(3)
γ (°)	90	90	90	90	90	90	90
Volume (Å^3)	3272.1(11)	3256.3(11)	1755.2(6)	1794.6(6)	1766.0(6)	6475(2)	3520.7(11)
Z	4	4	2	2	2	8	4
ρ_{calcd} (g cm^{-3})	1.417	1.603	1.331	1.383	1.571	1.568	1.393
μ(Mo Kα) (mm^{-1})	0.616	3.764	0.605	0.639	3.548	3.703	0.504
F(000)	1428	1566	728	764	828	3040	1520
Measured reflections	6104	5945	3436	3432	3445	5598	6531
Independent reflections	5801	5646	3218	3210	3229	5598	6211
Obs. reflections ($I > 2\sigma(I)$)	4660	4326	2417	2791	2914	2822	5005
R_1 ($F > 2\sigma(I)$)	0.0454	0.0545	0.0614	0.0587	0.0536	0.0949	0.0366
wR_2 (all data)	0.1242	0.1547	0.1799	0.1589	0.1412	0.2269	0.0944
Goodness-of-fit	1.063	1.100	1.037	1.066	1.079	0.947	1.049

In conclusion, this work shows that dotpm is an excellent chelating ligand. While similar in some respects to dppm when acting in this capacity, the enhanced steric bulk leading to restricted rotation about the carbon–phosphorus bonds potentially offers a more clearly defined reaction pocket at the metal centre. This can also be easily tuned upon modification of a backbone substituent leading to the facile synthesis of a wide range of derivatives with different spatial properties. In future work we aim to concentrate on the catalytic activity of Rdotpm and related ligands with other ortho substituents, particular focus being placed on group 8 and 10 complexes.

Experimental

All reactions were carried out under a nitrogen atmosphere in dried degassed solvents unless otherwise stated. *ortho*-Bromotoluene and P(*o*-tolyl)$_3$ were purchased from Aldrich and used as supplied, and (*o*-tolyl)$_2$PCl was prepared according to standard procedures (14). NMR spectra were run on Bruker AC300, AMX400, or Avance500 spectrometers and referenced internally to the residual solvent peak (^{1}H and ^{13}C) or externally to P(OMe)$_3$ (^{31}P). Infrared spectra were run on Nicolet 205 or Shimadzu 8700 FT-IR spectrometers. Solid-state spectra were recorded as KBr discs and solution spectra using a cell fitted with calcium fluoride plates, subtraction of the solvent absorptions being achieved by computation. The fast atom bombardment and electron impact mass spectra were recorded on a VG ZAB-SE high-resolution mass spectrometer in the Chemistry Department of University College London, and elemental analyses were performed in house. Chromatography was carried out on deactivated alumina (6% *w*/*w* distilled water) or silica wet packed with light petroleum unless otherwise stated. The solution to be separated was added to the support (3–5 g) and the solvent removed under reduced pressure. The resulting solids were then deposited on top of the prepared column and separation effected by elution with progressively more polar solvents.

Preparation of bis(di-*ortho*-tolylphosphino)methane (dotpm)

(*o*-Tolyl)$_2$PCl (13.17 g, 0.053 mol) was dissolved in dry THF (100 cm^3). Lithium metal (2.10 g, 0.265 mol) hammered and cut into strips was slowly added to the pale yellow solution. The mixture gradually turned blood red and was left to stir at room temperature for 20 h. After cooling to 0 °C, dry dichloromethane (1.7 cm^3, 0.027 mol) was slowly added, the solution turning brown. After 1 h the solution was warmed to room temperature and then refluxed for a further 1 h. After removal of volatiles, the yellow-brown solid produced was redissolved in dichloromethane and washed thoroughly with distilled water. The organic layer was dried over $MgSO_4$ and removal of volatiles under reduced pressure gave a cream solid (3.02 g, 26%). Recrystallization from dichloromethane and methanol afforded dotpm as white needles.

Alternatively, dotpm was also prepared by lithiation of P(*o*-tolyl)$_3$. P(*o*-tolyl)$_3$ (6.0 g, 0.0197 mol) was dissolved in dry THF (100 cm^3). Lithium metal (0.3 g) hammered and cut into strips was slowly added and the mixture was stirred for 20 h. Finely ground NH_4Br (1.96 g, 0.02 mol) was added in small portions to the blood red solution causing the mixture to autoreflux. After 2 h, dry dichloromethane (3 cm^3) was added dropwise and the color turned to pale straw. Approximately 30 cm^3 of methanol was added to remove any remaining lithium. After removal of volatiles under reduced pressure, dissolution of the residue in dichloromethane gave a colorless solution that was washed with distilled water several times and dried over $MgSO_4$. Removal of volatiles under reduced pressure gave dotpm (2.80 g, 65%). ^{1}H NMR ($CDCl_3$) δ: 7.36–7.10 (m, 16H, Ar), 2.60 (t, 2H, *J* = 2.5 Hz, CH_2), 2.30 (s, 12H, Me). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: –60.5 (s). Mass spectrum (EI) *m*/*z*: 440 [M$^+$], 425 [M$^+$ – CH_3], 349 [M$^+$ – *o*-tolyl). Anal. calcd. for $C_{29}H_{30}P_2 \cdot 0.5H_2O$: C 77.51, H 6.90, P 13.81; found: C 77.23, H 6.88, P 13.97.

Preparation of *cis*-[Cr(CO)$_4$(η^2-dotpm)] (1)

[$Cr(CO)_5Cl$][NEt_4] (0.59 g, 1.66 mmol) and dotpm (0.37 g, 0.83 mmol) were dissolved in dry dichloromethane (25 cm^3). The pale green solution was refluxed for 5 h and then filtered. The filtrate was washed thoroughly with distilled water and the dichloromethane extract was dried over $MgSO_4$. Removal of volatiles under reduced pressure yielded **1** as a yellow solid (0.37 g, 73%). IR ν(CO) (CH_2Cl_2, cm^{-1}): 2006 (s), 1896 (s), 1867 (s). ^{1}H NMR ($CDCl_3$) δ: 7.69 (dd, 4H, *J* = 12.4, 8.0 Hz, Ar), 7.30 (t, 4H, *J* = 7.4 Hz, Ar), 7.16 (t, 4H, *J* = 7.5 Hz, Ar), 7.11 (dd, 4H, *J* = 7.5, 1.0 Hz, Ar), 4.38 (t, 2H, *J* = 8.5 Hz, CH_2), 2.00 (s, 12H, Me). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 9.7 (s). Mass spectrum (FAB) *m*/*z*: 604 [M$^+$], 520 [M$^+$ – 3CO], 492 [M$^+$ – 4CO]. Anal. calcd. for $CrP_2O_4C_{33}H_{30}$: C 65.56, H 4.97, P 10.26; found: C 65.03, H 5.06, P 9.79.

Preparation of *cis*-[Mo(CO)$_4$(η^2-dotpm)] (2)

cis-[$Mo(CO)_4(pip)_2$] (0.10 g, 0.26 mmol) and dotpm (0.11 g, 0.26 mmol) were dissolved in dichloromethane (15 cm^3) and the orange solution was refluxed for 4 h. After cooling to room temperature, methanol (15 cm^3) was added and the solution was reduced under vacuum until a precipitate formed. The mixture was filtered and the residue washed with methanol and air-dried. The tan solid was recrystallized from dichloromethane and methanol to yield colorless crystals of **2** (0.10 g, 62%). IR ν(CO) (CH_2Cl_2, cm^{-1}): 2019 (s), 1909 (s), 1872 (s). ^{1}H NMR ($CDCl_3$) δ: 7.63 (dd, 4H, *J* = 13.2, 7.2 Hz, Ar), 7.29 (t, 4H, *J* = 7.5 Hz, Ar), 7.14 (t, 4H, *J* = 7.6 Hz, Ar), 7.11 (d, 4H, *J* = 7.6 Hz, Ar) 4.43 (t, 2H, *J* = 7.9 Hz, CH_2), 2.04 (s, 12H, Me). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: –14.2 (s). Mass spectrum (FAB) *m*/*z*: 650 [M$^+$], 623 [M$^+$ – CO], 594 [M$^+$ – 2CO], 538 [M$^+$ – 4CO]. Anal. calcd. for $MoP_2O_4C_{33}H_{30}$: C 61.11, H 4.63, P 9.57; found: C 60.41, H 4.77, P 9.15.

Preparation of *cis*-[W(CO)$_4$(η^2-dotpm)] (3)

cis-[$W(CO)_4(pip)_2$] (0.23 g, 0.49 mmol) and dotpm (0.22 g, 0.49 mmol) were dissolved in dichloromethane (15 cm^3) and the solution was refluxed for 2.5 h. The resulting yellow solution was pumped to dryness to yield a yellow solid, which was recrystallized from dichloromethane and methanol. Yellow crystals of **3** (0.24 g, 66%) were formed. IR ν(CO) (CH_2Cl_2, cm^{-1}): 2015 (s), 1900 (s), 1866 (s). ^{1}H NMR ($CDCl_3$) δ: 7.62 (dd, 4H, *J* = 13.9, 7.3 Hz, Ar), 7.30 (t,

4H, J = 7.4 Hz, Ar), 7.17 (t, 4H, J = 7.5 Hz, Ar), 7.12 (d, 4H, J = 7.2 Hz, Ar), 4.91 (t, 2H, J = 8.4 Hz, CH_2), 2.03 (s, 12H, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: –37.7 (s, J_{WP} = 197 Hz). Mass spectrum (FAB) *m/z*: 736 [M^+], 707 [M^+ – CO], 680 [M^+ – 2CO], 622 [M^+ – 4CO]. Anal. calcd. for $WP_2O_4C_{33}H_{30}\cdot 0.5CH_2Cl_2$: C 51.64, H 3.98, P 7.96; found: C 52.45, H 3.98, P 7.69.

Preparation of [CpRuCl(η²-dotpm)] (4)

[$CpRuCl(PPh_3)_2$] (0.37 g, 0.51 mmol) and dotpm (0.224 g, 0.51 mmol) were refluxed in toluene (100 cm^3) for 24 h. Chromatography on silica eluting with diethyl ether – light petroleum (2:1) gave a yellow band of [$CpRuCl(PPh_3)_2$], which was discarded. Eluting with diethyl ether – light petroleum (1:1) gave an orange band, which yielded **4** as an orange solid (0.14 g, 76%). IR (KBr, cm^{-1}): 1448 (m), 1132 (m), 1091 (m), 1089 (m), 1066 (m), 804 (m), 748 (s), 725 (s), 709 (m), 461 (s). ^1H NMR (CD_2Cl_2, 308 K) δ: 8.08 (br, 2H, Ar), 7.42–7.15 (m, 8H, Ar), 7.08 (d, 2H, J = 7.4 Hz, Ar), 7.04 (br d, 2H, Ar), 6.73 (t, 2H, J = 7.4 Hz, Ar), 4.94 (dt, 1H, J = 13.8, 8.1 Hz, CH_2), 4.75 (s, 5H, Cp), 4.54 (q, 1H, J = 10.9 Hz, CH_2), 2.08 (s, 6H, Me), 2.05 (s, 6H, Me); (228 K) δ: 8.51 (br, 1H, Ar), 7.58 (br, 1H, Ar), 7.40–6.95 (m, 11H, Ar), 6.86 (t, 1H, J = 7.1 Hz, Ar), 6.43 (br, 1H, Ar), 6.36 (br, 1H, Ar), 4.76 (br, 1H, CH_2), 4.75 (s, 5H, Cp), 4.46 (br, 1H, CH_2), 2.24 (s, 3H, Me), 2.13 (s, 3H, Me), 1.86 (s, 6H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: –4.7 (s). Mass spectrum (FAB) *m/z*: 642 [M^+], 607 [M^+ – Cl], 576 [M^+ – Cp]. Anal. calcd. for $C_{34}H_{35}P_2ClRu\cdot CHCl_3\cdot 2H_2O$: C 51.53, H 5.15; found: C 51.63, H 4.34.

Preparation of *cis*-[$PtCl_2$(η²-dotpm)] (5a)

cis-[$Pt(PhCN)_2Cl_2$] (0.21 g, 0.44 mmol) and dotpm (0.21 g, 0.44 mmol) were dissolved in dry dichloromethane (15 cm^3) and the solution was refluxed for 10 h. A white precipitate was formed and after cooling, hexane (ca. 15 cm^3) was added to precipitate more solids. The mixture was filtered and the residue was washed with hexane and air-dried. A white powder was obtained, which was recrystallized from dichloromethane and methanol to yield **5a** as colorless plates (0.28 g, 92%). IR ν(CH) (KBr, cm^{-1}): 3056 (w), 3011 (w), 2960 (w), 2919 (w), 2904 (w), 2856 (w). ^1H NMR ($CDCl_3$) δ: 7.96 (dd, 4H, J = 8.1, 7.9 Hz, Ar), 7.43 (t, 4H, J = 7.3 Hz, Ar), 7.23–7.20 (m, 8H, Ar), 4.59 (t, 2H, J = 10.0 Hz, CH_2), 2.26 (s, 12H, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: –77.9 (s, J_{PtP} = 3097 Hz). Mass spectrum (FAB) *m/z*: 1484 [$2M^+$+ 2Cl], 1409 [$2M^+$], 742 [M^+ + Cl], 671 [M^+ – Cl], 634 [M^+ – 2Cl]. Anal. calcd. for $PtP_2Cl_2C_{29}H_{30}$: C 49.29, H 4.25, Cl 10.06, P 8.78; found: C 48.70, H 4.08, Cl 10.75, P 8.48.

Preparation of *cis*-[$PtBr_2$(η²-dotpm)] (5b)

5a (0.05 g, 0.08 mmol) and LiBr (0.01 g, 0.15 mmol) were dissolved in dry THF (15 cm^3) and the mixture was stirred at room temperature for 20 h. The solvent was distilled off and the residue was redissolved in dichloromethane. This was washed thoroughly with distilled water and the dichloromethane extract was dried over $MgSO_4$. Removal of volatiles under reduced pressure gave **5b** as a yellow powder (0.05 g, 78%). ^1H NMR ($CDCl_3$) δ: 7.98 (q, 4H, J = 7.7 Hz, Ar), 7.44 (t, 4H, J = 7.3 Hz, Ar), 7.23–7.21 (m, 8H, Ar), 4.65 (t, 2H, J = 10.2 Hz, CH_2), 2.27 (s, 12H, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: –80.3 (s, J_{PtP} = 3056 Hz). Mass spectrum (FAB) *m/z*: 715 [M^+ – Br], 634 [M^+ – 2Br]. Anal. calcd. for $PtBr_2P_2C_{29}H_{30}\cdot CH_2Cl_2$: C 40.90, H 3.52, Br 18.18, P 7.04; found: C 40.92, H 4.44, Br 16.74, P 7.30.

Preparation of *cis*-[PtI_2(η²-dotpm)] (5c)

5a (0.05 g, 0.08 mmol) and LiI (0.02 g, 0.15 mmol) were dissolved in THF (15 cm^3) and the yellow solution was stirred at room temperature for 20 h. Removal of volatiles under reduced pressure yielded a yellow solid. This was redissolved in dichloromethane and was washed three times with water. The yellow solution was pumped to dryness under reduced pressure to give **5c** as a yellow powder (0.04 g, 62%). ^1H NMR ($CDCl_3$) δ: 7.97 (q, 4H, J = 7.7 Hz, Ar), 7.43 (t, 4H, J = 7.6 Hz, Ar), 7.23 (t, 8H, J = 7.7 Hz, Ar), 4.78 (t, 2H, J = 10.3 Hz, CH_2), 2.28 (s, 12H, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: –87.7 (s, J_{PtP} = 2876 Hz). Mass spectrum (FAB) *m/z*: 889 [M^+], 762 [M^+ – I]. Anal. calcd. for $PtP_2I_2C_{29}H_{30}$: C 39.15, H 3.37, I 28.57, P 6.97; found: C 39.08, H 3.69, I 28.63, P 7.18.

Preparation of *cis*-[$PdCl_2$(η²-dotpm)] (6)

cis-[$Pd(PhCN)_2Cl_2$] (0.16 g, 0.42 mmol) and dotpm (0.19 g, 0.42 mmol) were dissolved in dry dichloromethane (15 cm^3) and this was refluxed for 20 h. Removal of volatiles under reduced pressure gave **6** as a brown powder (0.19 g, 75%), which was washed with methanol and was air-dried. IR ν(CH) (KBr, cm^{-1}): 3055 (w), 2963 (w), 2920 (w). ^1H NMR ($CDCl_3$) δ: 7.97 (dd, 4H, J = 8.2 Hz, 7.7, Ar), 7.45 (t, 4H, J = 7.6 Hz, Ar), 7.23–7.19 (m, 8H, Ar), 4.33 (t, 2H, J = 9.9 Hz, CH_2), 2.32 (s, 12H, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: –69.0 (s). Mass spectrum (FAB) *m/z*: 583 [M^+ – Cl], 545 [M^+ – 2Cl]. Anal. calcd. for $PdP_2Cl_2C_{29}H_{30}\cdot 0.2$ PhCN: C 54.83, H 4.85, N 0.44, Cl 11.11, P 9.70; found: C 54.49, H 4.54, N 0.44, Cl 12.80, P 9.70.

Preparation of *cis*-[$Cr(CO)_4$(η²-Medotpm)] (7)

1 (0.33 g, 0.55 mmol) was dissolved in dry THF (25 cm^3). *n*-BuLi (0.7 cm^3, 1.09 mmol) was added and the yellow solution immediately darkened. After stirring at room temperature for 1 h, MeI (0.07 cm^3, 1.09 mmol) was added and the color lightened. The reaction mixture was stirred for 20 h and pumped to dryness under reduced pressure. The solid was redissolved in dichloromethane and was washed thoroughly with distilled water. The dichloromethane extract was dried over $MgSO_4$ and filtered. Removal of volatiles under reduced pressure yielded a yellow powder that was recrystallized from dichloromethane and methanol to give **7** as yellow crystals (0.33 g, 99%). IR ν(CO) (CH_2Cl_2, cm^{-1}): 2006 (s), 1913 (s), 1893 (s), 1865 (s). ^1H NMR ($CDCl_3$) δ: 8.27–8.26 (m, 4H, Ar), 7.38–7.33 (m, 8H, Ar), 7.05 (m, 4H, Ar), 5.39 (sextet, 1H, J = 7.2 Hz, CH), 2.09 (s, 6H, Me), 2.00 (s, 6H, Me), 1.06 (dt, 3H, J = 15.9, 7.3 Hz, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 27.8 (s). Mass spectrum (FAB) *m/z*: 618 [M^+], 562 [M^+ – 2CO], 534 [M^+ – 3CO], 506 [M^+ – 4CO]. Anal. calcd. for $CrP_2O_4C_{34}H_{32}\cdot 0.75CH_2Cl_2$: C 61.17, H 4.91, P 9.09; found: C 60.64, H 4.96, P 9.21.

Preparation of *cis*-[$Mo(CO)_4$(η²-Medotpm)] (8)

2 (0.30 g, 0.46 mmol) was dissolved in dry THF (15 cm^3). *n*-BuLi (0.37 cm^3, 0.60 mmol) was added to the yellow solu-

tion, which immediately turned darker and was stirred at room temperature for 1 h. MeI (0.04 cm^3, 0.60 mmol) diluted in dry THF (1 cm^3) was then added and the reaction mixture was stirred for 20 h, the color gradually lightening. Removal of volatiles under reduced pressure gave a yellow solid. This was redissolved in dichloromethane, washed thoroughly with distilled water, and dried over $MgSO_4$. Removal of volatiles under reduced pressure gave a yellow solid that was recrystallized from dichloromethane and methanol to give **8** as yellow crystals (0.18 g, 59%). IR ν(CO) (CH_2Cl_2, cm^{-1}): 2020 (s), 1921 (s), 1905 (s), 1869 (s). ^{1}H NMR ($CDCl_3$) δ: 8.14–8.10 (m, 4H, Ar), 7.33–7.22 (m, 8H, Ar), 7.08–7.06 (m, 4H, Ar), 5.38 (sextet, 1H, *J* = 7.7 Hz, CH), 2.14 (s, 6H, Me), 2.07 (s, 6H, Me), 1.08 (dt, 3H, *J* = 14.8, 7.7 Hz, Me). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 4.9 (s). Mass spectrum (FAB) *m/z*: 664 [M^+], 608 M^+ – 2CO], 552 [M^+ – 4CO]. Anal. calcd. for $MoP_2O_4C_{34}H_{32}\cdot 0.5CH_2Cl_2$: C 58.76, H 4.88, P 8.80; found: C 58.18, H 5.69, P 9.43.

Preparation of *cis*-[W(CO)$_4$(η^2-Medotpm)] (9)

3 (0.11 g, 0.15 mmol) was dissolved in THF (10 cm^3). *n*-BuLi (0.08 cm^3, 0.19 mmol) was added to the yellow solution, which immediately darkened. After 1 h, MeI (0.012 cm^3, 0.19 mmol) was added and the reaction stirred at room temperature for 20 h. After removal of volatiles under reduced pressure, redissolving in dichloromethane gave a yellow solution that was washed three times with water and dried over $MgSO_4$. Removal of volatiles under reduced pressure gave **9** as a yellow powder, which was recrystallized from dichloromethane and methanol to give yellow crystals (0.07 g, 62%). IR ν(CO) (CH_2Cl_2, cm^{-1}): 2016 (s), 1895 (s), 1863 (s). ^{1}H NMR ($CDCl_3$) δ: 8.17–8.11 (m, 4H, Ar), 7.37 (t, 2H, *J* = 7.3 Hz, Ar), 7.32 (t, 2H, *J* = 8.5 Hz, Ar), 7.28 (t, 2H, *J* = 8.3 Hz, Ar), 7.23 (t, 2H, *J* = 7.3 Hz, Ar), 7.06 (d, 2H, *J* = 8.0 Hz, Ar), 7.03 (d, 2H, *J* = 7.0 Hz, Ar), 6.01 (sextet, 1H, *J* = 7.3 Hz, CH), 2.11 (s, 6H, Me), 2.04 (s, 6H, Me), 1.02 (dt, 3H, *J* = 15.5, 7.7 Hz, Me). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: –18.0 (s, J_{WP} = 199 Hz). Mass spectrum (FAB) *m/z*: 750 [M^+], 722 [M^+ – CO], 694 [M^+ – 2CO], 666 [M^+ – 3CO], 636 [M^+ – 4CO – 2H]. Anal. calcd. for $WP_2O_4C_{34}H_{32}\cdot CH_2Cl_2$: C 50.30, H 4.07, P 7.43; found: C 50.23, H 4.01, P 7.46.

Preparation of [CpRuCl(η^2-Medotpm)] (10)

4 (0.10 g, 0.16 mmol) was dissolved in dry THF (5 cm^3) and ca. 0.16 mmol of $LiN(SiMe_3)_2$ was added dropwise. The solution was stirred for 20 h and 0.01 cm^3 of methyl iodide was added dropwise. After a further 2 h of stirring, volatiles were removed under reduced pressure and the residue redissolved in dichloromethane. This was washed with distilled water and dried with $MgSO_4$. Removal of volatiles under reduced pressure afforded **10** (0.07 g, 68%) as a slightly oily orange solid. ^{1}H NMR ($CDCl_3$, 298 K) δ: 8.3–6.2 (m, 16H, Ar), 5.21 (s, ca. 1.2H, Cp, **10b**), 5.15 (s, ca. 3.8H, Cp, **10a**), ca. 4.4 (vbr, 1H, CH), 2.60 (br, 6H, Me), 2.56 (br, 6H, Me), 0.90 (m, 3H, Me). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 20.5 (s, **10a**), 13.0 (s, **10b**). Mass spectrum (FAB) *m/z*: 656 [M^+], 621 [M^+ – Cl].

Preparation of *cis*-[PtI$_2$(η^2-Medotpm)] (11)

5a (0.178 g, 0.25 mmol) was dissolved in THF (5 cm^3) and $LiN(SiMe_3)_2$ (ca. 0.3 mmol) was added and the mixture was stirred for 20 h. MeI (0.016 cm^3, 0.26 mmol) was then added dropwise and the mixture was stirred for a further 2 h. Removal of volatiles under reduced pressure and redissolution in dichloromethane gave a yellow solution that was washed with distilled water and dried over $MgSO_4$. The volume of the extract was reduced (ca. 5 cm^3) under reduced pressure and **11** (0.156 g, 85%) was precipitated as a yellow solid upon addition of ethanol. ^{1}H NMR ($CDCl_3$) δ: 8.16 (br, 2H, Ar), 7.76 (br, 2H, Ar), 7.52–7.29 (m, 10H, Ar), 7.10 (br, 2H, Ar), 5.38 (dd, 1H, *J* = 18.7, 9.9 Hz, CH), 2.47 (br, 6H, CH_3), 2.34 (s, 6H, CH_3), 1.16 (dt, 3H, *J* = 20.5, 11.0 Hz, CH_3); ^{31}P{^{1}H} NMR ($CDCl_3$) δ: –71.4 (s, *J* = 2892 Hz). Mass spectrum (FAB) *m/z*: 903 [M^+], 776 [M^+ – I], 649 [M^+ – 2I]. Anal. calcd. for $C_{30}H_{32}I_2P_2Pt$: C 39.86, H 3.54; found: C 39.28, H 3.49.

Preparation of *cis*-[Mo(CO)$_4$(η^2-Etdotpm)] (12)

2 (0.33 g, 0.50 mmol) was dissolved in dry THF (25 cm^3) to form a pale yellow solution. *n*-BuLi (0.5 cm^3, 0.75 mmol) was added and the solution immediately darkened. After stirring at room temperature for 1 h, EtI (0.06 cm^3, 0.75 mmol) was added and the reaction mixture stirred for a further 20 h. The solvent was removed and the solid was redissolved in dichloromethane and washed thoroughly with distilled water. The dichloromethane extract was dried over $MgSO_4$ and the mixture was filtered. Removal of volatiles under reduced pressure gave **12** as a yellow solid (0.24 g, 72%). IR ν(CO) (CH_2Cl_2, cm^{-1}): 2018 (s), 1906 (s), 1870 (s). ^{1}H NMR (CD_2Cl_2, 308 K) δ: 7.99 (m, 2H, Ar), 7.87 (q, 2H, *J* = 7.5 Hz, Ar), 7.39 (t, 2H, *J* = 7.00 Hz, Ar), 7.33–7.27 (m, 4H, Ar), 7.24 (t, 2H, *J* = 7.4 Hz, Ar), 7.15 (d, 4H, *J* = 7.3 Hz, Ar), 4.83 (septet, 1H, *J* = 4.9 Hz, CH), 2.15 (s, 6H, Me), 2.08 (s, 6H, Me), 1.87 (doublet octets, 2H, *J* = 7.4 Hz, 5.1, CH_2), 0.78 (t, 3H, *J* = 7.4 Hz, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 5.9 (s). Mass spectrum (FAB) *m/z*: 678 [M^+], 664 [M^+ – Me], 649 [M^+ – Et], 622 [M^+ – 2CO], 566 [M^+ – 4CO]. Anal. calcd. for $MoP_2O_4C_{35}H_{34}$: C 62.13, H 5.03, P 9.17; found: C 62.16, H 5.55, P 10.85.

Preparation of *cis*-[W(CO)$_4$(η^2-Etdotpm)] (13)

3 (0.25 g, 0.35 mmol) was dissolved in dry THF (25cm^3) to form a pale yellow solution. *n*-BuLi (0.3 cm^3, 0.52 mmol) was added and the solution immediately darkened. This was left to stir at room temperature for 1 h. EtI (0.04 cm^3, 0.52 mmol) was then added and the solution was stirred for 20 h. The solvent was removed and the solid was redissolved in dichloromethane. This was washed thoroughly with distilled water. The dichloromethane extract was dried over $MgSO_4$ and the mixture was filtered. Removal of volatiles under reduced pressure gave a yellow powder. This was recrystallized from dichloromethane and methanol to give **13** as yellow crystals (0.19 g, 72%). IR ν(CO) (CH_2Cl_2, cm^{-1}): 2016 (s), 1900 (s), 1866 (s). ^{1}H NMR ($CDCl_3$) δ: 7.99 (m, 2H, Ar), 7.89 (q, 2H, *J* = 7.5 Hz, Ar), 7.34 (t, 4H, *J* = 7.2 Hz, Ar), 7.26 (m, 4H, Ar), 7.09 (m, 4H, Ar), 5.29 (br, 1H, CH), 2.13 (s, 6H, Me), 2.01 (s, 6H, Me), 1.81 (m, 2H, CH_2), 0.79 (t, 3H, *J* = 7.3 Hz, Me). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: –15.7 (s). Mass spectrum (FAB) *m/z*: 764 [M^+], 750 [M^+ – Me], 736 [M^+ – CO], 708 [M^+ – 2CO], 680 [M^+ –

3CO], 650 [M^+ – 4CO]. Anal. calcd. for $WP_2O_4C_{35}H_{34}$: C 54.97, H 4.45, P 8.12; found: C 54.36, H 4.84, P 7.51.

Preparation of *cis*-[Mo(CO)$_4$(η^2-Bzdotpm)] (14)

2 (0.33 g, 0.51 mmol) was dissolved in dry THF (25 cm^3). *n*-BuLi (0.5 cm^3, 0.77 mmol) was added and the solution immediately darkened. The reaction was stirred at room temperature for 1 h. Benzyl bromide (0.09 cm^3, 0.77 mmol) was added and the solution was stirred for another 20 h. The solvent was removed and the residue was redissolved in dichloromethane. This was washed thoroughly with distilled water. The organic layer was dried over $MgSO_4$ and the mixture was filtered. Removal of volatiles under reduced pressure gave an oil. This was recrystallized from dichloromethane and methanol to give **14** as yellow plates (0.13 g, 34%). IR ν(CO) (CH_2Cl_2, cm^{-1}): 2020 (s), 1898 (s), 1869 (s). ^{1}H NMR (CD_2Cl_2, 308 K) δ: 8.03 (q, 2H, *J* = 7.6 Hz, Ar_A), 7.93 (q, 2H, *J* = 7.0 Hz, Ar_B), 7.36 (t, 2H, *J* = 6.8 Hz, Ar_A), 7.31 (t, 2H, *J* = 6.4 Hz, Ar_B), 7.27 (t, 2H, *J* = 6.4 Hz, Ar_A), 7.21 (t, 2H, *J* = 7.4 Hz, Ar_B), 7.12 (dd, 2H, *J* = 7.5, 2.0 Hz, Ar_B), 7.08 (t, 1H, *J* = 7.2 Hz, Bz), 7.02 (t, 2H, *J* = 7.0 Hz, Bz), 6.96 (d, 2H, *J* = 7.0 Hz, Ar_A), 6.56 (d, 2H, *J* = 7.2 Hz, Bz), 5.53 (m, 1H, CH), 3.06 (dt, 2H, *J* = 14.2, 5.4 Hz, CH_2), 2.15 (s, 6H, Me_A), 1.82 (s, 6H, Me_B); (213 K) δ: 8.25 (br, 2H, Ar), 8.18 (br, 2H, Ar), 7.55–7.23 (m, 8H, Ar), 7.04 (brd, 2H, *J* = 6.7 Hz, Ar), 7.02 (t, 1H, *J* = 7.3 Hz, Bz), 6.92 (t, 2H, *J* = 7.1 Hz, Bz), 6.76 (brd, 2H, *J* = 6.8 Hz, Ar), 6.48 (d, 2H, *J* = 7.5 Hz, Bz), 5.80 (brs, 1H, CH), 2.84 (brdt, 2H, *J* = 14.9, 5.2 Hz, CH_2), 2.04 (brs, 6H, Me), 1.55 (brs, 6H, Me). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 6.9 (s). Mass spectrum (FAB) *m*/*z*: 740 [M^+], 713 [M^+ – CO], 684 [M^+ – 2CO], 628 [M^+ – 4CO]. Anal. calcd. for $MoP_2O_4C_{40}H_{36}\cdot 0.25CH_2Cl_2$: C 63.62, H 4.81, P 8.17; found: C 64.31, H 4.84, P 8.12.

Preparation of *cis*-[W(CO)$_4$(η^2-Bzdotpm)] (15)

3 (0.11 g, 0.15 mmol) was dissolved in dry THF (25 cm^3). *n*-BuLi (0.14 cm^3, 0.23 mmol) was added and the solution immediately darkened. The reaction was stirred at room temperature for 1 h. Benzyl bromide (0.03 cm^3, 0.23 mmol) was added and the solution was stirred for another 20 h. The solvent was removed and the residue was redissolved in dichloromethane. This was washed thoroughly with distilled water. The organic layer was dried over $MgSO_4$ and the mixture was filtered. Removal of volatiles under reduced pressure gave a yellow powder. This was recrystallized from dichloromethane and methanol to give **15** as yellow crystals (0.05 g, 40%). IR ν(CO) (CH_2Cl_2, cm^{-1}): 2016 (s), 1912 (s), 1896 (s), 1866 (s). ^{1}H NMR ($CDCl_3$) δ: 8.13 (brs, 2H, Ar), 8.02 (brs, 2H, Ar), 7.38–7.20 (m, 9H, Ar + Bz), 7.06 (d, 2H, *J* = 7.2 Hz, Ar), 7.00 (t, 2H, *J* = 7.7 Hz, Bz), 6.86 (d, 2H, *J* = 7.0 Hz, Ar), 6.55 (d, 2H, *J* = 7.3 Hz, Bz), 6.17 (brs, 1H, CH), 2.98 (dt, 2H, *J* = 15.0, 5.6 Hz, CH_2), 2.10 (s, 6H, Me), 1.71 (s, 6H, Me). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: –15.6 (s). Mass spectrum (FAB) *m*/*z*: 826 [M^+], 798 [M^+ – CO], 770 [M^+ – 2CO], 742 [M^+ – 3CO], 712 [M^+ – 4CO]. Anal. calcd. for $WP_2O_4C_{40}H_{36}$: C 58.11, H 4.36, P 7.51; found: C 57.67, H 4.20, P 7.40.

Preparation of [Mo(CO)$_3$(η^2-Medotpm)] (16)

8 (0.19 g, 0.28 mmol) was refluxed in xylene (15 cm^3) for 60 h. Removal of volatiles under reduced pressure gave a black solid (0.11 g, 62%). IR ν(CO) (CH_2Cl_2, cm^{-1}): 1901 (vs), 1840 (s). ^{1}H NMR ($CDCl_3$) δ: 7.41–6.98 (m, 16H, Ar), 3.27 (q, 1H, *J* = 7.1 Hz, CH), 2.49 (s, 6H, Me), 2.23 (s, 6H, Me), 0.97 (dt, 3H, *J* = 11.1, 4.0 Hz, Me). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: –46.7 (s). Mass spectrum (FAB) *m*/*z*: 606 [M^+ – CO], 592 [M^+ – Me – CO], 576 [M^+ – 2CO], 561 [M^+ – 2CO – Me], 552 [M^+ – 3CO].

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 an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo Kα radiation (λ = 0.710 73 Å) at 293 ± 2 K. Lattice parameters were identified by application of the automatic indexing routine of the diffractometer to the positions of a number of reflections taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure reflections and three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data was corrected for Lorenz and polarization effects and unique data with $I \geq 2\sigma(I)$ were used to solve and refine the structure. This was solved by direct methods and developed by using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically and placed in idealized positions (C—H, 0.96 Å) and assigned a common isotropic thermal parameter (U = 0.08 Å^2).[3]

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[3] Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5003. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 275347–275353 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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