result of the tendency of Li^+ and Cu^+ toward tetrahedral and linear coordination, respectively.

From the point of view of stoichiometry the structure of 1 is in broad agreement with the dimeric structure proposed for $LiCuMe_2$ in Et_2O. However, there are large differences in structural details. First, whereas $Li_2Cu_2Me_4$ was said to have approximate D_{2h} symmetry with coplanar Li, Cu, and Me groups, the organic groups of 1 show large deviations from the Li_2Cu_2 plane. Second, the Cu···Cu distance in $Li_2Cu_2Me_4$ was estimated to be 4.4 ± 0.7 Å,[13] which is very different from the value observed in 1. The validity of the 4.4-Å Cu···Cu distance has already been questioned and may be in error.[6,22] It is possible to argue that the deviation of the alkyl groups from the Li_2Cu_2 plane in 1 could be due to the steric effects of $-CH_2SiMe_3$. Nonetheless, it is notable that $Li_2Cu_2Ph_4$ (solvated by SMe_2)[21] also has a structure very similar to that of 1, whereas $Cu_4Ph_4(SMe_2)_2$[21] is almost planar, like $Cu_4(CH_2SiMe_3)_4$.[8] Thus, it appears that this intermediate structure in 1 may be more characteristic of $Li_2Cu_2R_4$ systems than the planar one proposed for $Li_2Cu_2Me_4$. It should also be borne in mind that, in solution, $Li_2Cu_2Me_4$ is probably solvated by ethers binding to lithium, which could play a role in its structure by imposing a nonplanar configuration on the molecule similar to that seen in 1.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for financial support.

Supplementary Material Available: Tables of crystal data, data collection, and refinement, atom coordinates, bond distances and angles, and thermal parameters (10 pages); a table of structure factors (18 pages). Ordering information is given on any current masthead page.

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Articles

Synthesis and Reactivity of "MoPt" Bimetallic Systems Containing the Ligand 2-Oxacyclopentylidene

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Oxidative addition of P–H bonds of primary/secondary phosphines, bound to Mo–2-oxacyclopentylidene systems, to Pt(0) complexes results in the transfer of the 2-oxacyclopentylidene ligand from the Mo to the Pt center. The cationic 2-oxacyclopentylidene complexes *cis*-$[Cp(OC)_2Mo(COCH_2CH_2CH_2)(PPh_2H)]BPh_4$ and *trans*-$[Cp(OC)_2Mo(COCH_2CH_2CH_2)(PCy_2H)]BPh_4$, obtained from the reaction of $Cp(OC)_3Mo(CH_2CH_2CH_2Br)$ with PR_2H and $NaBPh_4$, react (i) with $Pt(C_2H_4)_2(PCy_3)$ to give $[Cp(OC)_2Mo(\mu\text{-}PR_2)(\mu\text{-}H)Pt(COCH_2CH_2CH_2)(PCy_3)]BPh_4$ and (ii) with $Pt(C_2H_4)(PPh_3)_2$ to give equimolar mixtures of $[Cp(OC)_2Mo(\mu\text{-}PR_2)(\mu\text{-}H)Pt(COCH_2CH_2CH_2)(PPh_3)]BPh_4$, $Cp(OC)_2Mo(R_2PCOCH_2CH_2CH_2)$, and $[PtH(PPh_3)_3]BPh_4$. Reaction of $Cp(OC)_2Mo(COCH_2CH_2CH_2)(PCyH_2)]BPh_4$ with $Pt(C_2H_4)(PPh_3)_2$ gives a mixture of *trans(Mo),cis(Pt)*-$[Cp(OC)_2Mo(COCH_2CH_2CH_2)(\mu\text{-}PCyH)PtH(PPh_3)_2]BPh_4$ and $[Cp(OC)_2Mo(\mu\text{-}PCy(CHOCH_2CH_2CH_2))(\mu\text{-}H)Pt(PPh_3)_2]BPh_4$. The complexes $Cp(OC)_2Mo(R_2PCOCH_2CH_2CH_2)$ are readily obtained from the reaction of 7 or 8 with base (Proton Sponge). The molecular structure of $[Cp(OC)_2Mo(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(COCH_2CH_2CH_2)(PCy_3)]BPh_4\cdot CH_2Cl_2$ (**10a**) has been determined by single-crystal X-ray diffraction. Crystal data for **10a**: $C_{66}H_{76}BCl_2MoO_3P_2Pt$, fw = 1352.0, monoclinic, space group $P2_1/c$, $a = 17.920$ (3) Å, $b = 19.605$ (4) Å, $c = 18.301$ (3) Å, $\beta = 108.95$ (1)°, $V = 6081$ Å^3, $D_{exptl} = 1.48$ g cm^{-3} for $Z = 4$; $R(wR) = 0.052$ (0.051) for 5973 reflections with $F \geq 6\ \sigma(F)$. The structure of **10a** contains square-planar Pt and distorted 4:3 "piano-stool" Mo centers, which are linked by bridging diphenylphosphido and hydrido ligands with Pt–(μ-P)–Mo and Pt–(μ-H)–Mo bond angles of 81.28 (9) and 149 (7)°, respectively. The Pt···Mo separation (3.063 (1) Å) is long and weak.

Introduction

The oxidative addition of the P–H bond of a primary or secondary phosphine complex to Pt(0) complexes provides a synthetically useful route to a wide range of single-phosphido-bridged heterobimetallic complexes.[1-5] An early example involves the reaction of $(OC)_5M(PR_2H)$ (**1**; M = Cr, Mo, W) with $Pt(C_2H_4)(PPh_3)_2$ to give the μ-

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[1] Powell, J.; Gregg, M. R.; Sawyer, J. F. *J. Chem. Soc., Chem. Commun.* 1984, 1149; *Inorg. Chem.* 1989, *28*, 4451.

[2] Powell, J.; Sawyer, J. F.; Smith, S. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1312.

[3] Powell, J.; Sawyer, J. F.; Stainer, M. V. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1314; *Inorg. Chem.* **1989**, *28*, 4461.

[4] Schwald, J.; Peringer, P. *J. Organomet. Chem.* 1987, *323*, C51.

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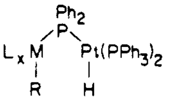
Table I. IR Data (ν_{CO} Region (cm^{-1}), CH_2Cl_2 Solution) for the Complexes *cis*- (7) and *trans*-$[Cp(OC)_2Mo(COCH_2CH_2CH_2CH_2)(PR_2H)]BF_4$ (8) and $Cp(OC)_2Mo(R_2PCOCH_2CH_2CH_2)$ (9) {PR_2 = PPh_2 (a), PCy_2 (b), PCyH (c)}

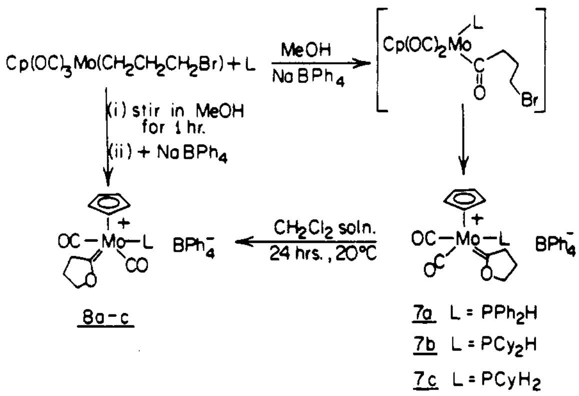
7a	7c	8a	8b	8c	9a	9b	9c
1996 (s)	1991 (s)	1992 (m)	1990 (m)	1994 (m)	1945 (s)	1934 (s)	1940 (s)
1930 (s)	1920 (s)	1913 (s)	1911 (s)	1915 (s)	1864 (s)	1860 (s)	1857 (s)

phosphido derivative $(OC)_5M(\mu\text{-}PPh_2)PtH(PPh_3)_2$ (2).[1] Facile loss of CO from the 18-electron M center in 2 is platinum-assisted (a clear example of a cooperativity effect), the CO being transferred to the Pt center (via intermediates 3 and 4; Scheme I) prior to loss from the molecule with formation of the μ-phosphido–μ-hydrido complex $(OC)_4M(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2$ (5) as the isolable final product. Extension of this synthetic procedure has been used to study CO, H, and μ-PR_2 ligand labilities, protonation–deprotonation processes, and cluster assembly and cluster rearrangement processes in a range of "M_xPt_y" heterobimetallics (x = 1–3, y = 1–3).[1-7] Of particular interest is the utilization of this synthetic approach for the generation of complexes of the type $L_x(R)M(\mu\text{-}PPh_2)Pt(H)(PPh_3)_2$ (6). Of note is the close proximity of an organic group R (on M) to the hydrido ligand (on Pt) in 6, and the study of such systems may provide useful information with regard to intramolecular ligand reactivities and the nature of cooperativity effects in bimetallic systems.



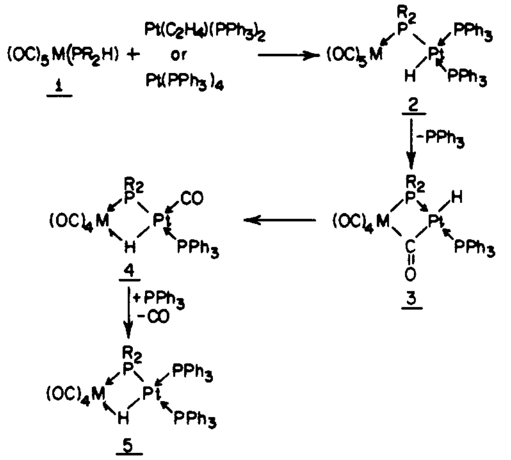
6

In this paper we report the synthesis of the primary and secondary phosphine complexes *cis*- and *trans*-$[Cp(OC)_2Mo(COCH_2CH_2CH_2)(PR_2H)]BPh_4$ (7 (cis), 8 (trans); PR_2H = PPh_2H, PCy_2H, $PCyH_2$), which have been obtained (eq 1) by following the procedure described by Cotton and Lukehart[8] for the preparation of $[Cp(OC)_2Mo(COCH_2CH_2CH_2)(PPh_3)]BPh_4$. Subsequent reactions of the complexes 7 and 8 with $Pt(C_2H_4)(PPh_3)_2$ and $Pt(C_2H_4)_2(PCy_3)$ are described, and carbene ligand (2-oxacyclopentylidene) transfer from Mo to Pt or from Mo to μ-P via Pt (for the primary phosphine complexes) is shown to be a dominant feature of the chemistry of these systems.



(1)

Scheme I



Results

The preparation/isolation of the cyclic (2-oxycarbene)(phosphine)molydenum complexes $[Cp(OC)_2Mo(COCH_2CH_2CH_2)(PR_2H)]^+$ (cation of 7; cis configuration) involves the addition of the appropriate primary or secondary phosphine to a MeOH solution of $Cp(CO)_3Mo(CH_2CH_2CH_2Br)$ in the presence of excess $NaBPh_4$ (eq 1). For the addition of PPh_2H and $PCyH_2$ the presence of the large counterion BPh_4^- causes a rapid precipitation of the initially formed cis complexes 7a and 7c, which are isolated as yellow powders essentially free of any contamination with the trans isomers 8. For PCy_2H rapid precipitation of *cis*-$[Cp(OC)_2Mo(COCH_2CH_2CH_2)(PCy_2H)]BPh_4$ does not occur and only the trans product 8b (the product of a relatively rapid (20 min) intramolecular cis → trans isomerization[8,9]) may be isolated in pure form. The cis complexes 7a and 7c isomerized cleanly and completely to the trans isomers 8a and 8c when stirred in CH_2Cl_2 solution for 24 h. The relative intensities of the two ν_{CO} absorptions are useful indicators of the cis (7) or trans (8) stereochemistry of $[Cp(OC)_2Mo(COCH_2CH_2CH_2)(PR_2H)]BPh_4$ (Table I).[8]

The P–H bonds in 7 and 8 are relatively acidic and are readily deprotonated by Proton Sponge (1,8-bis(dimethylamino)naphthalene) to give the complexes $Cp(OC)_2Mo(PR_2COCH_2CH_2CH_2)$ (9), in which the (presumed) initially formed phosphide has reacted with (nucleophilic addition to) the 2-oxacyclopentylidene ligand (eq 2). The structure of 9 is similar to that of the "ylide complex" $(OC)_4Mn(PPh_2CR(OSiMe_3))$.[10]

Reaction of $[Cp(CO)_2Mo(COCH_2CH_2CH_2)(PR_2H)]BPh_4$ with $Pt(C_2H_4)_2(PCy_3)$. The oxidative addition of the P–H bond of *cis*-$[Cp(OC)_2Mo(COCH_2CH_2CH_2)(PPh_2H)]BPh_4$ (7a) to $Pt(C_2H_4)_2(PCy_3)$ leads to the μ-phosphido–μ-hydrido cationic complex $[Cp(OC)_2Mo(\mu\text{-}$

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(5) Powell, J.; Gregg, M. R.; Sawyer, J. F. *J. Chem. Soc., Chem. Commun.* **1987**, 1029; *Inorg. Chem.* **1988**, *27*, 4521.

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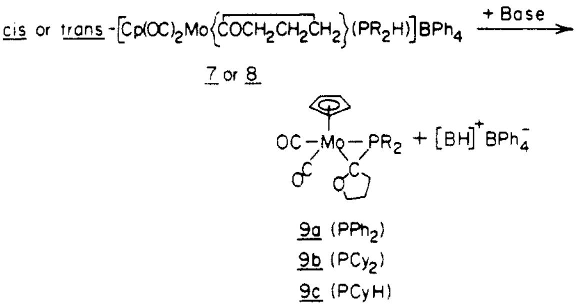
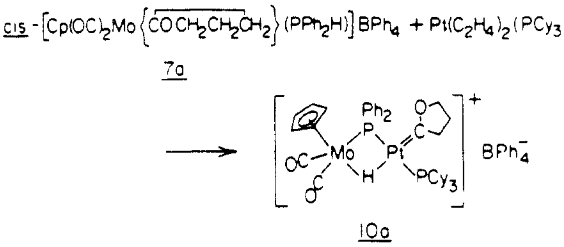


(2)

PPh$_2$)(μ-H)Pt($\overline{\text{COCH}_2\text{CH}_2\text{CH}_2}$)(PCy$_3$)]BPh$_4$ (**10a**) as the sole product (eq 3). The reaction is essentially complete within 30 min (20 °C), and no intermediate species were observed (NMR monitoring; CD$_2$Cl$_2$). The solution structure of [Cp(OC)$_2$Mo(μ-PPh$_2$)(μ-H)Pt($\overline{\text{COCH}_2\text{CH}_2\text{CH}_2}$)(PCy$_3$)]BPh$_4$ (**10a**) is based on ^{1}H and ^{31}P{^{1}H} NMR and IR data (Table II). The magnitude of the $^1J_{^{195}\text{Pt}-^1\text{H}}$ coupling to the hydrido ligand (338 Hz) is consistent with a bridged hydride,[11] the downfield shift of δ_{P_μ} implies a small ∠PtPMo angle,[12,13] the large $^2J_{^{31}\text{P}-^{31}\text{P}}$ coupling (181 Hz) implies a trans arrangement of the two P donor ligands on Pt, and the relative intensities of the two ν_{CO} absorptions (I_{1970}/I_{1900} = 1.48) are consistent with a "*cis*-(CO)$_2$" orientation at Mo.[8] The ^{1}H NMR resonances of the 2-oxacyclopentylidene ligand are broader in **10a** then in **7a**, suggestive of carbene transfer to Pt (additional ^{195}Pt coupling). The molecular structure of **10a** as determined by single-crystal X-ray diffration[14] confirms these structural features, including the locations of the 2-oxacyclopentylidene ligand on the Pt and the hydrido bridge (Figure 1).



(3)

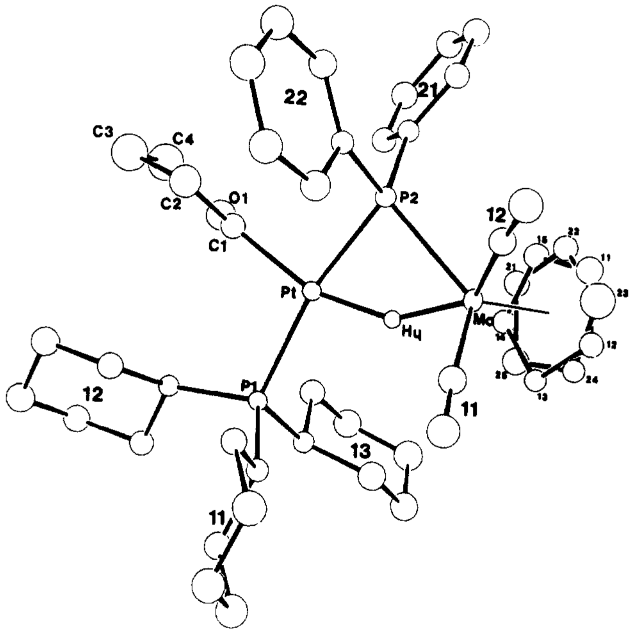
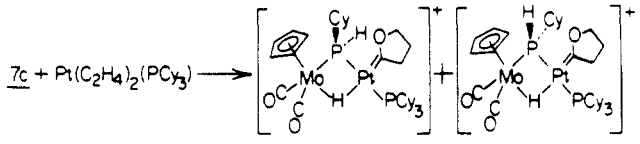


Figure 1. Molecular structure of [Cp(OC)$_2$Mo(μ-PPh$_2$)(μ-H)Pt($\overline{\text{COCH}_2\text{CH}_2\text{CH}_2}$)(PCy$_3$)]BPh$_4$ (**10a**).

The reaction of *trans*-[Cp(CO)$_2$Mo($\overline{\text{COCH}_2\text{CH}_2\text{CH}_2}$)(PCy$_2$H)]BPh$_4$ (**8b**) with Pt(C$_2$H$_4$)$_2$(PCy$_3$) proceeds similarly, though considerably more slowly than eq 3 (24-h reaction time), to give [Cp(OC)$_2$Mo(μ-PCy$_2$)(μ-H)Pt($\overline{\text{COCH}_2\text{CH}_2\text{CH}_2}$)(PCy$_3$)]BPh$_4$ (**10b**). The reaction of the primary phosphine complex *cis*-[Cp(OC)$_2$Mo($\overline{\text{COCH}_2\text{CH}_2\text{CH}_2}$)(PCyH$_2$)]BPh$_4$ (**7c**) with Pt(C$_2$H$_4$)$_2$(PCy$_3$) is rapid (reaction complete within 2 min) and gives [Cp(OC)$_2$Mo(μ-PCyH)(μ-H)Pt($\overline{\text{COCH}_2\text{CH}_2\text{CH}_2}$)(PCy$_3$)]BPh$_4$ as ca. a 4:1 mixture of the diastereomers **10c** and **10c′** (eq 4; see Table II for NMR and IR data). The assigned stereochemistry of **10c** and **10c′** is arbitrary. It has not been determined whether or not the **10c**:**10c′** ratio is kinetically or thermodynamically controlled. It should be noted that a cis → trans → cis rearrangement at Mo of the type observed in Cp(OC)$_2$MoXL systems[17] could provide a **10c** ⇄ **10c′** equilibration pathway.



cation of **10c** cation of **10c′**

(4)

The Reaction of [Cp(OC)$_2$Mo($\overline{\text{COCH}_2\text{CH}_2\text{CH}_2}$)(PR$_2$H)]BPh$_4$ with Pt(C$_2$H$_4$)(PPh$_3$)$_2$ in CH$_2$Cl$_2$ (or CD$_2$Cl$_2$) occurs as outlined in eq 5 to give equimolar amounts of Cp(OC)$_2$Mo(μ-PR$_2$)(μ-H)Pt($\overline{\text{COCH}_2\text{CH}_2\text{CH}_2}$)(PPh$_3$) (**11a,b**), the ylide complexes **9a,b**, and the cationic hydride [PtH(PPh$_3$)$_3$]BPh$_4$ (**12**). These complexes (which can be separately isolated from solution) are readily identified and characterized spectroscopically (Table I and Experimental Section). The complex hydride [PtH(PPh$_3$)$_3$]BPh$_4$ (**12**) is readily identified by its unusual

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(11) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415.

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(14) C$_{66}$H$_{76}$BCl$_2$MoO$_3$P$_2$Pt (**10a**), Fw = 1352.03, is monoclinic, space group $P2_1/c$, with a = 17.920 (3) Å, b = 19.605 (4) Å, c = 18.301 (3) Å, β = 108.95 (1)°, V = 6081 Å^3, D_{exptl} = 1.48 g cm^{-3} for Z = 4, λ(Mo Kα) = 0.71069 Å, μ = 27.1 cm^{-1}8 $F(000)$ = 2740, and T = 298 K. Unit cell dimensions are based on 25 reflections (10.8 < θ < 16.4°). Intensity data collection (Enraf-Nonius CAD4 diffractometer; ω–2θ scans over scan range (0.65 + 0.35 tan θ)°; maximum scan time 65 s; 3 standards every 8500 s) gave 11355 data in quadrants $h,k,\pm l$ with 2θ ≤ 50° (total includes standards and only 0kl data). Lorentz, polarization, crystal decay (maximum decay in intensity −12.6%), and absorption corrections (needle-shaped crystal; faces [distances, cm] {100} [0.0105], {010} [0.0043], (001) [0.0068], (001) [0.0033], and (011) [0.0026]; 12 × 6 × 8 grid; transmission range 0.666–0.842) were applied to all data collected. The structure was solved by use of Patterson (Pt + Mo), least-squares, Fourier, and ΔF Fourier techniques. H atoms were placed in calculated positions or located in ΔF maps. A molecule of CH$_2$Cl$_2$ solvent and μ-H between Pt and Mo were located in the ΔF map and refined. Blocked least-squares minimizing $\sum w\Delta F^2$ converged to R = 0.0522 (R_w = 0.0512) for 5973 reflections with $F \geq 6\sigma(F)$ (7 reflections with bad $w\Delta F^2$ values were deemed to have been mismeasured and were rejected from the final cycles). $w = [\sigma^2(F) + 0.000614F^2]^{-1}$. Maximum residual peaks were ≤1.21 e Å^{-3} near Pt. Programs: Enraf-Nonius SDP package and SHELX on PDP 11/23 and Gould 9705 computers.[15] Scattering factors were from ref 16.

(15) Enraf-Nonius Structure Determination Package; B. A. Frenz and Associates: College Station, TX. Sheldrick, G. M. SHELX-Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

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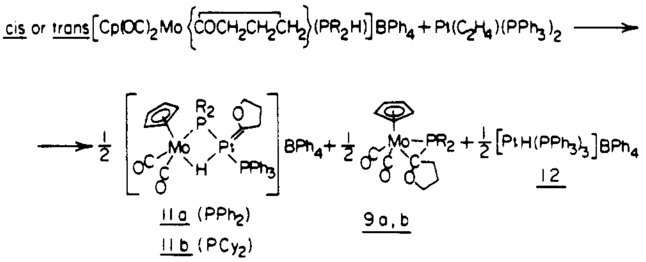
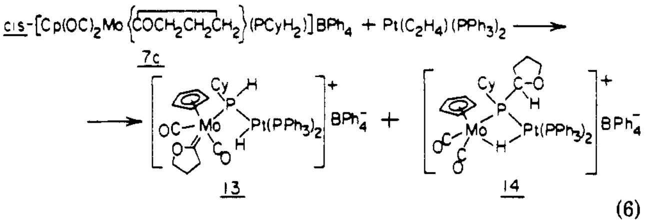


(5)

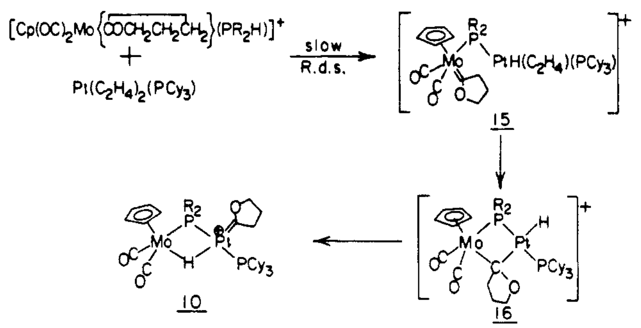
^{1}H NMR spectrum.[18] The reaction of *cis*-[Cp(OC)$_2$Mo(COCH$_2$CH$_2$CH$_2$)(PPh$_2$H)]BPh$_4$ (**7a**) and Pt(PPh$_3$)$_4$ proceeds to give an equimolar mixture of *cis*-Cp(OC)$_2$Mo(PPh$_2$COCH$_2$CH$_2$CH$_2$) (**9a**) and [PtH(PPh$_3$)$_3$]BPh$_4$ only (i.e. a simple proton transfer).

The reaction of the primary phosphine complex *cis*-[Cp(OC)$_2$Mo(COCH$_2$CH$_2$CH$_2$)(PCyH$_2$)]BPh$_4$ (**7c**) with Pt(C$_2$H$_4$)(PPh$_3$)$_2$ is more complex and proceeds to give a ca. 1:1 mixture of the terminal and bridged platinum hydrides *trans(Mo),cis(Pt)*-[Cp(OC)$_2$(COCH$_2$CH$_2$CH$_2$)Mo(μ-PCyH)PtH(PPh$_3$)$_2$]BPh$_4$ (**13**) and *cis*-[Cp(OC)$_2$Mo(μ-PCy(CHOCH$_2$CH$_2$CH$_2$)(μ-H)Pt(PPh$_3$)$_2$]BPh$_4$ (**14**), respectively, as the major products (eq. 6). The CH$_2$Cl$_2$ solution IR spectrum contains two strong ν_{CO} absorptions at 1970 and 1895 cm^{-1}. The relative intensities of these bands are consistent with a mixture of *trans*-“(OC)$_2$Mo” (**13**) and *cis*-“(OC)$_2$Mo” (**14**) moieties. The structural assignment of **13** is based on an analysis of its ^{1}H and ^{31}P{^{1}H} NMR data (Table III). The hydrido ligand is coupled to two distinct cis and one trans ^{31}P nuclei, and the magnitudes of $^1J_{^{195}\mathrm{Pt}-^1\mathrm{H}}$ (893 Hz) and $^2J_{^{31}\mathrm{P(trans\ to\ H)}-^1\mathrm{H}}$ (166 Hz) are consistent with a terminal hydrido structure. The ^{31}P{^{1}H} NMR spectrum contains resonance patterns assignable to three distinct P donor ligands attached to Pt. The upfield shift of the phosphido ligand (δ_{P_μ} = 27.2 ppm; $^1J_{^{31}\mathrm{P}-^1\mathrm{H}}$ = 310 Hz; proton-coupled spectrum) implies an unsupported μ-PCyH bridge.[12,13] Since **14** has a *cis*-“(OC)$_2$Mo” structure (see below), it follows that **13** has a trans orientation of the carbonyl ligands about Mo. The ^{1}H NMR spectrum of **14** (Table III) contains a hydrido resonance typical of a bridging hydride ($^1J_{^{195}\mathrm{Pt}-^1\mathrm{H}}$ = 515 Hz) coupled to three P donor ligands with $^2J_{^{31}\mathrm{P(trans\ to\ H)}-^1\mathrm{H}}$ (76 Hz) typical of a μ-H system. The downfield shift of the bridging phosphido ligand (δ_{P_μ} = 214 ppm) implies a small ∠PtPMo (~80°; see **10a**, Figure 1). The proton-coupled ^{31}P NMR spectrum (Table III) confirms the absence of a P–H bond on the phosphido bridge of **14**. We postulate that **14** contains a cyclohexyl(2-oxacyclopentyl)phosphido bridge as shown. The ^{1}H NMR spectrum of **14** (after partial separation from **13**) exhibits resonances attributable to the 2-oxacyclopentyl moiety at 3.78 ppm (OCH$_2$), 3.56 ppm ($J_{^{31}\mathrm{P}-^1\mathrm{H}}$ = 12 Hz, CH), 3.47 ppm (CHCH_2), and 2.66 ppm (CH$_2$CH_2CH$_2$). Attempts to grow crystals of **14** suitable for X-ray diffraction were not successful.



(6)

Scheme II



Upon closer examination of the ^{1}H NMR spectrum (hydrido region) of the 1:1 solution mixture of **13** and **14** obtained from **7c** and Pt(C$_2$H$_4$)(PPh$_3$)$_2$ (eq 6) an additional minor resonance pattern is observed with chemical shifts and coupling constants vary close to (i.e. overlapping with) those of **14**. We suggest that this second bridged hydride, **14′** (ratio **14**:**14′** = ca. 15:1), is a diastereomer associated with the asymmetric centers μ-P and the “yl” C atom of the 2-oxacyclopentyl group. (Note that in **10c** and **10c′** (enantiomers associated with the asymmetric Mo and P centers) a much larger difference in δ_H of the hydrido ligand is observed ($\Delta\delta_H$ = 0.8 ppm for **10c**, **10c′** as compared with 0.01 ppm for **14**, **14′**).) The reaction of *trans*-[Cp(OC)$_2$Mo(COCH$_2$CH$_2$CH$_2$)(PCyH$_2$)]BPh$_4$ (**8c**) with Pt(C$_2$H$_4$)(PPh$_3$)$_2$ gives the terminal hydride **13** (ν_{CO} = 1973 (m), 1897 (s) cm^{-1}).

Discussion

Mechanism(s) of the Reaction of [Cp(OC)$_2$Mo(COCH$_2$CH$_2$CH$_2$)(PR$_2$H)]BPh$_4$ with Pt(0) Complexes. While the cations [Cp(OC)$_3$M(PPh$_2$H)]$^+$ (M = Mo, W) react with Pt(C$_2$H$_4$)(PPh$_3$)$_2$ to give MPt bimetallic complexes via a mechanism involving deprotonation–reprotonation pathways,[2,7] such is not the case with the carbene cations [Cp(OC)$_2$Mo(COCH$_2$CH$_2$CH$_2$)(PR$_2$H)]$^+$. Evidence that this is so is the reaction of Pt(PPh$_3$)$_4$ with **7a** to give the ylide complex **9a** and [PtH(PPh$_3$)$_3$]$^+$ and the observation that **9a** does not react further with either Pt(C$_2$H$_4$)(PPh$_3$)$_2$ or [PtH(PPh$_3$)$_3$]$^+$. The fact that *trans*-[Cp(OC)$_2$Mo(COCH$_2$CH$_2$CH$_2$)(PCyH$_2$)]BPh$_4$ (**8c**) reacts with Pt(C$_2$H$_4$)(PPh$_3$)$_2$ to give [Cp(OC)$_2$(COCH$_2$CH$_2$CH$_2$)Mo(μ-PCyH)PtH(PPh$_3$)$_2$]BPh$_4$ (**13**) points to oxidative addition of a P–H bond across Pt to be the likely initial step in the formation of all the MoPt bimetallic complexes described herein. The possibility that the initial reactions involve addition of “Pt(PR$_3$)$_x$” to the carbene moiety (similar to the reactions described and studied by Stone et al.[19]) seems unlikely in view of the formation of **13** and the fact that the trans complexes **8** are less reactive than the cis complexes **7** with regard to the formation of **10**, **11**, and **14**. For addition of Pt directly to a carbene one would expect the trans isomers to be more sterically accessible and reactive. A plausible mechanism for the formation of the complexes **10** involves an initial rate-determining oxidative addition of the P–H bond to Pt to give **15**, followed by rapid carbene transfer via the μ-2-oxacyclopentylidene derivative **16** (Scheme II). Known complexes containing a 2-oxycarbene bridge include (OC)$_5$W(C(OMe)Ph)Pt(PMe$_3$)$_2$ and Cp(CO)$_2$Mn-

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Table II. ^1H (Hydride Ligand) and $^{31}P\{^1H\}$ NMR Data (CD_2Cl_2 Solution, δ (ppm), J (Hz)) and IR Data (cm^{-1}, CH_2Cl_2 Solution) for $[Cp(OC)_2Mo(\mu\text{-}PR_2)(\mu\text{-}H)Pt(\overline{COCH_2CH_2CH_2})(PR'_3)]BPh_4$ (10) and 11

complex	μ-PR_2	PR'_3	δ_H	$^1J_{^{195}Pt-^1H}$	$^2J_{^{31}P-^1H}$	δ_{P_μ}	$^1J_{^{195}Pt-^{31}P_\mu}$	$\delta_{PR'_3}$	$^1J_{^{195}Pt-^{31}P}$	$^2J_{^{31}P-^{31}P}$	ν_{CO}	
10a	PPh_2	PCy_3	−12.0	338	23.6, 10.8	149	1435	33	2516	181	1970 (s)	1900 (s)
10b	PCy_2	PCy_3	−12.9	331	23.1, 11.7	189	1513	29	2417	164	1963 (s)	1890 (s)
10c	PCyH	PCy_3	−12.6	330	23.9, 11.2	110	1470	32	2526	168	1968 (s)	1898 (s)
10c′	PCyH	PCy_3	−12.9	330	23.9, 11.1	126	1472	~32	~2520	168		
11a	PPh_2	PPh_3	−11.1	348	23.3, 11.8	156	1733	16	2558	195	1972 (s)	1904 (s)
11b	PCy_2	PPh_3	−12.0	341	22.1, 12.7	198	1616	14	2456	173	1964 (s)	1896 (s)

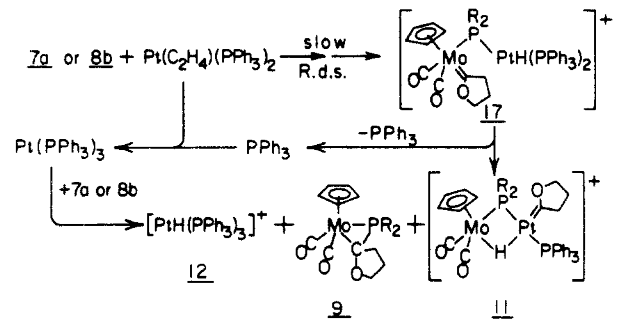
Table III. ^1H (Hydride Ligand) and $^{31}P\{^1H\}$ NMR Data (CD_2Cl_2 Solution; δ (ppm), J (Hz)) and IR Data (cm^{-1}, CH_2Cl_2 Solution) for $[Cp(OC)_2(\overline{COCH_2CH_2CH_2})Mo(\mu\text{-}PCyH)PtH(PPh_3)_2]BPh_4$ (13) and $[Cp(OC)_2Mo(\mu\text{-}PCy(\overline{CHOCH_2CH_2CH_2}))(\mu\text{-}H)Pt(PPh_3)_2]BPh_4$ (14)[a]

complex	ν_{CO}		δ_H	$^1J_{^{195}Pt-^1H}$	$^2J_{^{31}P-^1H}$
13	1972 (m)	1895 (s)	−4.90	874	166, 25.4, 17.6
14	1968 (s)	1896 (s)	−10.46[b]	515	76, 22.3, 16.5

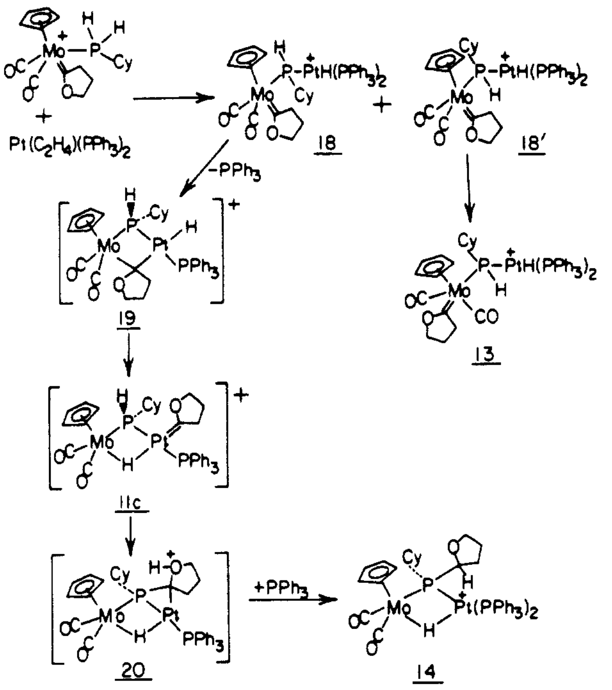
complex	δ_{P_μ}	$\delta_{P^aPh_3}$	$\delta_{P^bPh_3}$	$^1J_{^{195}Pt-^{31}P_\mu}$	$^1J_{^{195}Pt-^{31}P^a}$	$^1J_{^{195}Pt-^{31}P^b}$	$^2J_{^{31}P_\mu-^{31}P^a}$	$^2J_{^{31}P_\mu-^{31}P^b}$	$^2J_{^{31}P^a-^{31}P^b}$
13	−27.2	27.3	21.1	1963	2157	2463	0	298	17
14	214.4	20.8	11.0	1660	2500	2390	0	193	20

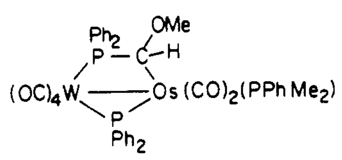
[a] P^a = PPh_3 cis to μ-P; P^b = PPh_3 trans to μ-P. [b] Overlaps a very minor resonance pattern at δ_H −10.47 with *J*'s similar to those of to **14**.

Scheme III



Scheme IV





21

$(\overline{C(OMe)Ph)Pt}(PMe_3)_2$,[19] and 2-oxacyclopentylidene ligand transfer from Mn to Pt has been previously observed in the reaction of $Mn(\overline{COCH_2CH_2CH_2})I(CO)_4$ with $Pt(C_2H_4)_2(P^tBu_2Me)$.[20] Formation of a bridging 2-oxacyclopentylidene intermediate has been postulated to account for the fluxional nature of $\overline{(OC)_3Mo(\eta^5,\eta^5\text{-}fulvalene)Mo}(CO)_2(\overline{COCH_2CH_2CH_2})$.[21] The reaction of *cis*- or *trans*-$[Cp(OC)_2Mo(\overline{COCH_2CH_2CH_2})(PR_2H)]BPh_4$ with $Pt(C_2H_4)(PPh_3)_2$ can be considered to proceed similarly to give **11** (structural analogues of **10**) with displacement of a PPh_3 ligand, which then reacts with $Pt(C_2H_4)(PPh_3)_2$ to give $Pt(PPh_3)_3$ (Scheme III). $Pt(PPh_3)_3$ is sufficiently basic to deprotonate a molecule of **7a**/**8b** to yield complex **9** and $[PtH(PPh_3)_3]BPh_4$ (Scheme III). The formation of the two complexes **13** and **14** from the reaction of the primary phosphine complex **7c** (eq 6) likewise involves oxidative addition, but the presence of diastereotopic P–H's can now lead to the pair of terminal Pt hydrides **18** and **18′** (Scheme IV). However, in this case the rate of carbene transfer to Pt via **19** is not as fast as for the μ-PCy_2 and μ-PPh_2 systems and cis to trans isomerization about Mo can proceed at a competitive rate. (NB The complex $(OC)_5Mo(\mu\text{-}PPh_2)PtH(PPh_3)_2$ (**2**; Scheme I) readily loses CO via Pt to give $(OC)_4Mo(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2$ (**5**),[1] while the phenylphosphide analogue $(OC)_5Mo(\mu\text{-}PPhH)PtH(PPh_3)_2$ is much more stable and can be isolated without CO loss.[4] This difference in reactivity can be rationalized in terms of the Thorp–Ingold effect on ring (μ-CO or μ-carbene) formation.[1]) A consideration of steric effects in the possible carbene-bridged intermediates suggests that **18** should more readily lead to carbene transfer than **18′**. Presumably **18′** is the primary source of the terminal hydride **13**, though some could arise from **18**. The intermediate **18** is postulated to reorganize, with transfer of the carbene ligand to Pt occurring via **19** to give **11c** and PPh_3. Carbene ligand transfer from Pt to P then occurs to give the observed product **14**. The postulated intermediate **20** is structurally similar to the com-

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(21) Drage, J. S.; Vollhardt, K. P. C. *Organometallics* **1985**, *4*, 191.

Table IV. Final Atomic Positional (×10⁴, ×10⁵ for Pt, Mo) and Thermal (×10³ Å²) Parameters of 10a

atom	x	y	z	U or U_{eq}
Pt	28038 (2)	22280 (2)	1601 (2)	27.4 (2)[a]
Mo	30714 (5)	9952 (5)	−7528 (5)	31.9 (5)[a]
P(1)	3824 (2)	3033 (1)	531 (2)	30.4 (16)[a]
P(2)	1960 (2)	1356 (1)	−371 (2)	30.5 (17)[a]
Cl(1S)	9777 (4)	4463 (3)	1919 (4)	159 (6)[a]
Cl(2S)	8726 (4)	5573 (3)	1427 (4)	154 (6)[a]
C(1S)	8860 (11)	4701 (10)	1366 (11)	117 (6)
O(1)	2221 (6)	2642 (5)	1356 (5)	77 (3)
O(11)	3487 (5)	1903 (5)	−1956 (5)	70 (3)
O(12)	1710 (5)	635 (5)	−2244 (5)	73 (3)
C(1)	2069 (7)	2661 (6)	602 (7)	49 (3)
C(2)	1317 (9)	2982 (8)	224 (8)	77 (4)
C(3)	1087 (10)	3312 (9)	902 (10)	106 (6)
C(4)	1544 (11)	2958 (10)	1544 (11)	115 (6)
C(11)	3330 (7)	1577 (6)	−1484 (7)	53 (3)
C(12)	2206 (7)	786 (6)	−1674 (7)	50 (3)
Cp(11)[b]	328 (2)	−18 (1)	−67 (2)	55 (7)
Cp(12)[b]	387 (2)	11 (1)	−88 (1)	45 (6)
Cp(13)[b]	433 (1)	56 (1)	−26 (2)	37 (5)
Cp(14)[b]	397 (2)	51 (1)	37 (1)	43 (5)
Cp(15)[b]	331 (2)	6 (2)	8 (2)	52 (7)
Cp(21)[c]	362 (3)	27 (3)	32 (2)	53 (10)
Cp(22)[c]	316 (2)	−13 (2)	−31 (3)	48 (9)
Cp(23)[c]	349 (4)	−9 (3)	−89 (3)	90 (18)
Cp(24)[c]	415 (2)	29 (2)	−69 (3)	39 (9)
Cp(25)[c]	428 (2)	59 (2)	13 (3)	57 (10)
C(111)	4030 (6)	3350 (5)	−333 (6)	38 (3)
C(112)	3314 (6)	3515 (6)	−1025 (6)	47 (3)
C(113)	3560 (8)	3650 (7)	−1737 (8)	74 (4)
C(114)	4152 (8)	4195 (7)	−1597 (8)	70 (4)
C(115)	4871 (8)	4057 (7)	−922 (8)	71 (4)
C(116)	4652 (7)	3928 (6)	−199 (7)	54 (3)
C(121)	3596 (6)	3747 (5)	1092 (6)	36 (3)
C(122)	2948 (7)	4220 (6)	610 (7)	52 (3)
C(123)	2690 (8)	4703 (7)	1123 (8)	65 (4)
C(124)	3373 (8)	5125 (7)	1632 (8)	70 (4)
C(125)	4031 (8)	4683 (7)	2096 (7)	63 (4)
C(126)	4312 (7)	4174 (6)	1597 (7)	51 (3)
C(131)	4756 (6)	2687 (5)	1158 (6)	39 (3)
C(132)	4648 (7)	2335 (7)	1869 (7)	58 (3)
C(133)	5412 (9)	2032 (7)	2381 (8)	75 (4)
C(134)	5830 (9)	1594 (8)	1997 (9)	82 (5)
C(135)	5944 (8)	1934 (7)	1312 (8)	69 (4)
C(136)	5165 (8)	2220 (7)	754 (7)	66 (4)
C(211)	1683 (6)	788 (5)	271 (6)	38 (3)
C(212)	1231 (7)	224 (6)	−4 (7)	49 (3)
C(213)	1067 (7)	−237 (7)	497 (7)	59 (4)
C(214)	1356 (7)	−147 (7)	1262 (7)	60 (4)
C(215)	1804 (8)	402 (7)	1561 (7)	63 (4)
C(216)	1995 (7)	870 (6)	1081 (7)	51 (3)
C(221)	1044 (6)	1689 (5)	−1034 (6)	37 (3)
C(222)	1109 (7)	2146 (6)	−1591 (7)	57 (3)
C(223)	437 (8)	2501 (7)	−2065 (8)	68 (4)
C(224)	−226 (8)	2391 (7)	−1957 (8)	72 (4)
C(225)	−336 (8)	1946 (7)	−1419 (8)	70 (4)
C(226)	317 (7)	1602 (6)	−948 (7)	53 (3)
B(1)	7873 (8)	2577 (7)	34 (7)	44 (3)
C(1A)	7136 (6)	2117 (5)	−496 (6)	44 (3)
C(2A)	7253 (8)	1597 (7)	−996 (7)	62 (4)
C(3A)	6651 (9)	1186 (7)	−1412 (8)	74 (4)
C(4A)	5919 (8)	1279 (7)	−1416 (8)	70 (4)
C(5A)	5745 (9)	1767 (8)	−992 (8)	77 (4)
C(6A)	6360 (7)	2201 (7)	−531 (7)	61 (3)
C(1B)	7597 (6)	3096 (6)	599 (6)	41 (3)
C(2B)	7100 (7)	3649 (6)	293 (7)	57 (3)
C(3B)	6835 (8)	4089 (7)	740 (8)	69 (4)
C(4B)	7039 (8)	4002 (7)	1530 (8)	71 (4)
C(5B)	7536 (8)	3456 (8)	1862 (8)	75 (4)
C(6B)	7777 (7)	3023 (7)	1389 (7)	62 (4)
C(1C)	8204 (6)	3079 (6)	−531 (6)	44 (3)
C(2C)	8828 (8)	3533 (7)	−182 (7)	65 (4)
C(3C)	9113 (9)	3989 (8)	−641 (9)	82 (4)
C(4C)	8779 (9)	3972 (8)	−1423 (9)	80 (4)
C(5C)	8190 (8)	3537 (8)	−1784 (8)	77 (4)
C(6C)	7911 (7)	3090 (7)	−1319 (7)	60 (3)
C(1D)	8563 (7)	2043 (5)	536 (6)	44 (3)
C(2D)	8358 (7)	1560 (6)	998 (7)	55 (3)
C(3D)	8881 (8)	1089 (7)	1447 (8)	66 (4)
C(4D)	9648 (8)	1091 (7)	1453 (8)	65 (4)
C(5D)	9859 (8)	1545 (7)	991 (7)	63 (4)
C(6D)	9337 (7)	2018 (6)	545 (7)	51 (3)
H(1)	3143 (53)	1686 (47)	−338 (52)	46 (28)

[a] U_{eq} value for anisotropically refined atom; $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)$. [b] Population parameter 0.60. [c] Population parameter 0.40.

plex 21, which is the product of a carbene–phosphido bridge coupling reaction.[22]

Molecular Structure of 10a. An ORTEP drawing with labeling scheme is given in Figure 1. Tables IV–VI list positional parameters and bond length and bond angle data. The structure of 10a contains a planar PtMo(μ-P)(μ-H) unit in which the Pt⋯Mo separation is 3.063 (1) Å. This distance is longer than the heterobimetallic Pt–Mo distances tabulated by Bender et al.[23] (2.651 (4)–2.912 (4) Å) and the Pt–Mo bond length (2.766 (1) Å) in $(Et_3P)Pt(\mu\text{-}PPh_2)_2Mo(CO)_4$.[24] However, in the present structure the μ-H position, which was located and refined, results in 10a containing a much more linear Pt(μ-H)Mo arrangement (Pt–(μ-H)–Mo = 149 (7)°) than has been found in other Pt heterobimetallics and hydrogen-bridged molybdenum systems.[25] Furthermore, the observed Pt–(μ-H) (1.64 (10) Å) and Mo–(μ-H) (1.54 (9) Å) distances, although somewhat inaccurate, are shorter than typical values quoted by Teller and Bau.[25] However, the large range of Mo–(μ-H) distances there (1.52 (3)–2.19 (6) Å) and more recent results from these laboratories[1–3,5–7] on other platinum heterobimetallics have indicated that distances involving bridging hydrogens will be significantly affected by other geometrical requirements of the metals and the nature of the counterion. Similar comments have been

Table V. Selected Bond Distances (Å)

Pt–Mo	3.063 (1)
Pt–P(1)	2.342 (3)
Pt–P(2)	2.280 (3)
Pt–C(1)	1.950 (14)
Pt–H(1)	1.64 (10)
Mo–P(2)	2.420 (3)
Mo–H(1)	1.54 (9)
Mo–C(11)	1.926 (14)
Mo–C(12)	1.927 (11)
Mo–Cp(11)	2.33 (3)
Mo–Cp(12)	2.31 (3)
Mo–Cp(13)	2.30 (2)
Mo–Cp(14)	2.37 (2)
Mo–Cp(15)	2.34 (3)
Mo–Cp(21)	2.37 (4)
Mo–Cp(22)	2.34 (4)
Mo–Cp(23)	2.29 (6)
Mo–Cp(24)	2.35 (4)
Mo–Cp(25)	2.38 (4)
P(1)–C(111)	1.84 (1)
P(1)–C(121)	1.86 (1)
P(1)–C(131)	1.82 (1)
P(2)–C(211)	1.80 (1)
P(2)–C(221)	1.82 (2)
C(1S)–Cl(1S)	1.69 (2)
C(1S)–Cl(2S)	1.73 (2)
O(1)–C(1)	1.32 (2)
O(1)–C(4)	1.50 (2)
C(1)–C(2)	1.44 (2)
C(2)–C(3)	1.57 (3)
C(3)–C(4)	1.38 (2)
C(11)–O(11)	1.18 (2)
C(12)–O(12)	1.17 (1)
Cp(11)–Cp(12)	1.35 (5)
Cp(11)–Cp(15)	1.42 (6)
Cp(12)–Cp(13)	1.47 (4)
Cp(13)–Cp(14)	1.50 (5)
Cp(14)–Cp(15)	1.44 (4)
Cp(21)–Cp(22)	1.43 (6)
Cp(21)–Cp(25)	1.47 (8)
Cp(22)–Cp(23)	1.37 (9)
Cp(23)–Cp(24)	1.35 (8)
Cp(24)–Cp(25)	1.55 (7)

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Table VI. Selected Bond Angles (deg)

Mo–Pt–P(1)	116.36 (8)	C(12)–Mo–Cp(11)	85.2 (8)
–P(2)	51.33 (8)	–Cp(12)	95.6 (7)
–C(1)	144.7 (3)	–Cp(13)	132.2 (8)
–H(1)	15 (3)	–Cp(14)	143.5 (7)
P(1)–Pt–P(2)	167.3 (1)	–Cp(15)	109.1 (8)
–C(1)	98.9 (3)	Pt–P(1)–C(111)	109.5 (3)
–H(1)	102 (3)	–C(121)	112.1 (4)
P(2)–Pt–C(1)	93.4 (3)	–C(131)	113.7 (4)
–H(1)	66 (3)	C(111)–P(1)–C(121)	111.1 (5)
C(1)–Pt–H(1)	159 (3)	–C(131)	105.5 (5)
Pt–Mo–P(2)	47.38 (7)	C(121)–P(1)–C(131)	104.7 (5)
–H(1)	16 (4)	Pt–P(2)–Mo	81.28 (9)
–C(11)	91.5 (4)	–C(211)	118.1 (3)
–C(12)	114.9 (4)	–C(221)	110.2 (4)
–Cp(11)	142.6 (10)	Mo–P(2)–C(211)	115.7 (4)
–Cp(12)	149.4 (6)	–C(221)	124.2 (4)
–Cp(13)	112.6 (7)	C(211)–P(2)–C(221)	106.1 (5)
–Cp(14)	91.4 (6)	Pt–H(1)–Mo	149 (7)
–Cp(15)	107.2 (10)	Cl(1S)–C(1S)–Cl(2S)	111.1 (10)
P(2)–Mo–H(1)	63 (4)	Pt–C(1)–O(1)	119.0 (8)
–C(11)	115.7 (4)	–C(2)	130 (1)
–C(12)	79.1 (4)	O(1)–C(1)–C(2)	111 (1)
–Cp(11)	113.7 (9)	C(1)–O(1)–C(4)	109 (1)
–Cp(12)	147.5 (9)	C(1)–C(2)–C(3)	104 (1)
–Cp(13)	142.0 (9)	C(2)–C(3)–C(4)	103 (2)
–Cp(14)	105.0 (8)	C(3)–C(4)–O(1)	108 (2)
–Cp(15)	92.2 (10)	Mo–C(11)–O(11)	176 (1)
H(1)–Mo–C(11)	80 (4)	Mo–C(12)–O(12)	176 (1)
–C(12)	122 (3)	Cp(15)–Cp(11)–Cp(12)	111 (3)
–Cp(11)	148 (3)	Cp(11)–Cp(12)–Cp(13)	109 (3)
–Cp(12)	139 (3)	Cp(12)–Cp(13)–Cp(14)	107 (2)
–Cp(13)	103 (3)	Cp(13)–Cp(14)–Cp(15)	105 (2)
–Cp(14)	90 (3)	Cp(14)–Cp(15)–Cp(11)	109 (2)
–Cp(15)	114 (4)	Cp(25)–Cp(21)–Cp(22)	110 (4)
C(11)–Mo–C(12)	80.0 (5)	Cp(21)–Cp(22)–Cp(23)	108 (4)
–Cp(11)	124.1 (11)	Cp(22)–Cp(23)–Cp(24)	113 (5)
–Cp(12)	94.5 (9)	Cp(23)–Cp(24)–Cp(25)	108 (5)
–Cp(13)	93.6 (9)	Cp(24)–Cp(25)–Cp(21)	101 (3)
–Cp(14)	126.4 (9)		
–Cp(15)	152.1 (10)		

made for $(\mu\text{-H})(\mu\text{-Ph}_2\text{P(CH}_2)_n\text{PPh}_2)\text{Mo}_2(\text{CO})_8^-$ salts.[26] The bridging hydrogen in **10a** is approximately trans (159 (3)°) to the carbon atom of the 2-oxacyclopentylidene ligand and completes a square-planar geometry at platinum. Likewise, along with the μ-P atom, two carbonyls, and the three vertices occupied by the cyclopentadienyl ligand, the bridging hydride completes a distorted 4:3 piano-stool geometry at molybdenum with the Cp ring as the seat. At Pt the angles C(1)–Pt–P(1) (98.9 (3)°) and P(1)–Pt–(μ-H) (102 (3)°) indicate that the C(1) and μ-H atoms are bent toward the bridging phosphorus atom. Consistent with the long Pt–Mo distance, the angle at μ-P is somewhat larger (81.28 (9)°) than that in other systems.[23,24] In **10a** the Mo–(μ-P) distance of 2.420 (3) Å is slightly shorter than the Mo–P distance of 2.473 (3) Å reported for *trans*-CpMo(MeCO)(CO)$_2$(PPh$_3$)[27] but is comparable to the Mo–P distance of 2.417 (5) Å in the complex $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\overline{\text{Mo(CO)}_2(\mu\text{-dppm})\text{Pt}}(\text{dppm})]^+[\text{Mo}_2\text{O}_7]^{2-})_{1/2}$.[28] These distances are substantially shorter than other Mo–P distances involving bulky phosphines.

The distance from Mo to the centroid of the Cp ring (which is disordered in a 60:40 ratio over two sites) and the Mo–CO distances in **10a** (1.991, 1.926 (14), and 1.927 (11) Å, respectively) are shorter than comparable distances in the complex $(\text{Et}_3\text{P})_2(\text{H})\text{PtMoCp(CO)}_3$[29] (2.060 (1) Å for Mo···Ct and 1.93 (1)–1.97 (1) Å for the three Mo–CO distances), while in the 4:3 piano-stool geometry of the $\text{CpMo(CO)}_2(\text{PMe}_3)_2^+$ cation the Mo–P, Mo–Cp, and Mo–CO distances are 2.468 (4), 2.29–2.37 (2), and 1.97 (2) Å, respectively.[30] No semibridging character for the CO's in **10a** is observable, and the Mo—C≡O angles are close to 180°.

The observed Pt–C(1) distance (1.950 (14) Å) to the 2-oxacyclopentylidene ligand is shorter than the corresponding distance (2.00 (2) Å) to this ligand in *trans*-methyl(2-oxacyclopentylidene)bis(dimethylphenylphosphine)platinum(II) hexafluorophosphate[31] but somewhat longer than that (1.889 (8) Å) in [tetracarbonyl(μ_2-iodo)(methyldi-*tert*-butylphosphine)(2-oxacyclopentylidene)platinum]manganese.[20] In this last compound the ∠PPtC angle (98.2 (3)°) is very similar to the present ∠P(1)PtC(1) angle (98.9 (3)°). Bond angles at C(1) in **10a** are very unsymmetrical (Pt–C(1)–O = 119.0 (8)° and Pt–C(1)–C(5) = 129.9 (10)°) but are generally comparable to values observed in the above oxacyclopentylidene systems.

The lattice of **10a** also contains BPh_4^- anions and dichloromethane solvent with C–Cl = 1.69 (2) and 1.74 (2) Å (Cl–C–Cl = 111.1 (10)°). The BPh_4^- anion is slightly "stretched" away from tetrahedral symmetry with angles between the *ad* and *bc* rings of 107.2 (9) and 105.4 (9)° and other angles of 109.8–111.6 (9)°. This is also reflected in differences of 3.4, 4.6, 6.0, and 8.6°, respectively, in the pairs of B–C–C angles for each of the *a*, *b*, *c*, and *d* rings and C–C$_\alpha$–C angles of 113.7–116.4 (12)°.

Experimental Section

All manipulations were carried out under an atmosphere of dry N$_2$ with use of dry degassed solvents. IR spectra (as CH$_2$Cl$_2$ solutions) were recorded on a Nicolet 10DX spectrometer. ^{1}H and ^{31}P{^{1}H} NMR spectrda (CD$_2$Cl$_2$) were obtained on a Varian XL200 spectrometer and are referenced to TMS and 85% H$_3$PO$_4$, respectively. Elemental analyses were performed by Canadian Microanalytical Laboratories, Vancouver, BC, Canada.

PPh$_2$H, PCy$_2$H, and PCyH$_2$ were obtained from Strem Chemicals Inc. Proton Sponge (1,8-bis(dimethylamino)naphthalene) was obtained from Aldrich. The complexes Cp(OC)$_3$Mo(CH$_2$CH$_2$CH$_2$Br),[32] Pt(C$_2$H$_4$)(PPh$_3$)$_2$,[33] and Pt(C$_2$H$_4$)$_2$(PCy$_3$)[34] were prepared by literature methods.

Preparations. ***cis*-[Cp(OC)$_2$Mo($\overline{\text{COCH}_2\text{CH}_2\text{CH}_2}$)(PPh$_2$H)]BPh$_4$ (7a).** To a stirred solution of Cp(OC)$_3$Mo(CH$_2$CH$_2$CH$_2$Br) (0.636 g, 1.73 mmol) and NaBPh$_4$ (0.777 g, 2.27 mmol) in MeOH (25 mL) was added PPh$_2$H (0.40 mL). After 5 min the resultant yellow precipitate was allowed to settle and the mother liquor removed by syringe. The yellow solid was washed with Et$_2$O (3 × 50 mL) and dried under vacuum to give **7a** as a light and air-sensitive yellow powder, 60% yield. Anal. Calcd (found) for C$_{47}$H$_{42}$BMoO$_3$P: C, 71.26 (70.84); H, 5.30 (5.05). ^{1}H NMR: Cp, δ 5.34 (1:1 doublet, $J_{^{31}\text{P}-^1\text{H}}$ = 1.5 Hz); OCH_2, δ 4.51 (broad 1:3:3:1 quartet) and δ 4.26 (broad 1:3:3:1 quartet, OCH_2 protons are diastereotopic); CCH_2, δ 2.85 (broad multiplet); CH$_2$CH_2CH$_2$, δ 1.24 (multiplet); PH, δ 6.72 (1:1 doublet, $J_{^{31}\text{P}-^1\text{H}}$ = 378 Hz). When it stands in CH$_2$Cl$_2$ solution, **7a** slowly isomerizes (24 h) to *trans*-[Cp(OC)$_2$Mo($\overline{\text{COCH}_2\text{CH}_2\text{CH}_2}$)(PPh$_2$H)]BPh$_4$ (**8a**). ^{1}H NMR: Cp, δ 5.49 (singlet); OCH_2, δ 4.79 (1:2:1 triplet); CCH_2, δ 3.50 (1:2:1 triplet); CH$_2$CH_2CH$_2$, δ 1.83 (multiplet).

The complex *cis*-[Cp(OC)$_2$Mo($\overline{\text{COCH}_2\text{CH}_2\text{CH}_2}$)(PCyH$_2$)]BPh$_4$ (**7c**) was similarly prepared. Anal. Calcd (found) for C$_{41}$H$_{44}$BMoO$_3$P: C, 68.16 (67.93); H, 6.14 (6.20).

Reaction of PCy$_2$H with Cp(OC)$_3$Mo(CH$_2$CH$_2$CH$_2$Br) and NaBPh$_4$ gave the trans product **8b** on workup. Anal. Calcd

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(found) for $C_{47}H_{54}BMoO_3P$: C, 70.15 (70.32); H, 6.76 (6.68).

$Cp(OC)_2Mo(Ph_2PCOCH_2CH_2CH_2)$ (9a). To a solution of **7a** (0.191 g) in CH_2Cl_2 (6 mL) was added Proton Sponge (0.69 g, 1.34 equiv). The solvent was removed (in vacuo) and the residue column chromotographed on Fluorisil by eluting with CH_2Cl_2–hexane (50:50). Addition of hexane to the eluate precipitated **9a** as a yellow powder (0.063 g, 55%). Anal. Calcd (found) for $C_{23}H_{21}MoO_3P$: C, 58.49 (57.91); H, 4.48 (4.57). ^1H NMR: Cp, δ 5.24 (singlet); OCH_2, δ 3.98 (1:3:3:1 quartet); CCH_2, δ 3.29 (broad multiplet); $CH_2CH_2CH_2$, δ 2.31 (broad multiplet). Complexes **9b** and **9c** could be prepared in similar yields from **8b** and **7c**. Reaction of **8b** with Proton Sponge required 3 h at 20 °C, probably because of a high activation energy associated with a trans to cis isomerization prior to the formation of **9b**. Anal. Calcd (found) for $C_{23}H_{33}MoO_3P$ (**9b**): C, 57.03 (56.62); H, 6.87 (6.55). Calcd (found) for $C_{17}H_{23}MoO_3P$ (**9c**): C, 50.76 (50.34); H, 5.76 (5.40).

$[Cp(OC)_2Mo(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(COCH_2CH_2CH_2)(PCy_3)]BPh_4$ (10a). $Pt(C_2H_4)_2(PCy_3)$ (0.176 g, 0.33 mmol) was added to a solution of **7a** (0.273 g, 0.34 mmol) in CH_2Cl_2 (10 mL). After 1 h the solvent was removed (in vacuo) and the residue redissolved in a minimum volume of acetone. Addition of hexane gave **10a** as a yellow powder (0.360 g, 83% yield). Recrystallization from CH_2Cl_2–hexane gave yellow prisms suitable for X-ray diffraction. Anal. Calcd (found) for $C_{65}H_{75}BMoO_3P_2Pt\cdot CH_2Cl_2$: C, 58.59 (58.13); H, 5.96 (5.89). The cationic dimers **10b** and **10c** were similarly prepared (70–80% yields). Anal. Calcd (found) for $C_{65}H_{87}BMoOP_2Pt$ (**10b**): C, 60.98 (60.73); H, 6.85 (6.62). Complex **10b** exhibited an unusually large separation of the diastereotopic OCH_2 proton resonances. ^1H NMR: Cp, δ 5.39; OCH_2, δ 4.98 and 4.76 (broad multiplets); CCH_2, δ 3.48 and 3.38 (broad multiplets); $CH_2CH_2CH_2$, resonances masked by Cy proton resonances.

The reactions of **7** and **8** with $Pt(C_2H_4)(PPh_3)_2$ were carried out in NMR tubes (CD_2Cl_2 solutions). Attempts to separate **13** and **14** were not completely successful.

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Supplementary Material Available: Tables A–C, containing hydrogen atom positions, anisotropic thermal parameters, and bond lengths and bond angles in the cyclohexyl and phenyl groups and BPh_4^- anion (4 pages); Table D, containing final structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

Reactions of $HC{\equiv}CCMe_2NHCOR$ Alkynes with $M_3(CO)_{12}$ Carbonyls ($M = Ru$, $R = C_6H_9$, Ph; $M = Os$, $R = C_6H_9$). Synthesis and Crystal Structure of $Ru_4(CO)_{11}(HC{\equiv}CCMe_2NHCOC_6H_9)$, a Butterfly Cluster Showing an Interaction between a Wingtip Metal and the Amide CO

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The alkynes $HC{\equiv}CCMe_2NHCOR$ react with $M_3(CO)_{12}$ (M = Ru or Os) giving, upon oxidative addition, the expected hydrides $(\mu\text{-}H)M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CCMe_2NHCOR)$ and the unprecedented butterfly clusters $M_4(CO)_{11}(\mu_4\text{-}\eta^2\text{-}HC{\equiv}CCMe_2NHCOR)$. These complexes have been characterized by spectroscopic studies; the structure of the ruthenium butterfly cluster with $R = C_6H_9$ has been determined by X-ray diffraction methods. Crystals, containing $CHCl_3$ as solvation molecules, are triclinic with $Z = 2$ in a unit cell of dimensions $a = 13.521$ (6), $b = 14.617$ (6), $c = 9.049$ (5) Å, $\alpha = 79.28$ (2), $\beta = 108.79$ (2), $\gamma = 111.85$ (2)°. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least-squares to $R = 0.0425$ for 4586 observed reflections. The organic ligand interacts with all the metals of the butterfly cluster in a $\mu_4\text{-}\eta^2$ fashion through the alkyne moiety and with a wingtip metal through the amide CO group. Evidence has been obtained for the formation of the butterfly clusters via metal fragment condensation on the $HM_3(CO)_9(C{\equiv}CCMe_2NHCOR)$ clusters, which may be obtained in a retrosynthetic pattern via protonation of the butterfly derivatives.

Introduction

The reactions of $Ru_3(CO)_{12}$ with alkynes lead to different cluster substitution products depending on the nature of the alkyne;[1] for example, with C_2Ph_2, the butterfly cluster $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)$ (1)[2] is obtained via "metal fragment condensation", whereas other internal aliphatic alkynes such as C_2Et_2 undergo oxidative addition and form isomeric (allenic or allylic) $HRu_3(CO)_9(C_6H_9)$ derivatives.[3]

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