reaction, culminating in the cleavage of the Co–C bond and transfer of the organo group to the reduced attacking metal. This reaction mechanism is reminiscent of the reactions by $I_2$ and other electrophiles on organometallic compounds of Pb and Sn, which were shown to occur by charge-transfer complexation, electron transfer to form a radical pair, and finally transfer of the organo group to the electrophile within the radical pair.[25] The sequence of steps for the platinum–$CH_3$-$B_{12}$ reaction is similar, but the nature of the interactions is qualitatively different. The $CH_3$-$B_{12}$···$Pt^{II}$ intermediate, for example, is probably not a charge-transfer complex of the traditional definition. And, whereas electron transfer from $R_4Pb$ or $R_4Sn$ occurs from a carbon–metal orbital, the electron transferred from $CH_3$-$B_{12}$ to platinum probably does not. Thus, the breaking of the Co–C bond arises from interactions elsewhere in the molecule and not directly on the Co–C bond. This may have implications for the mechanisms of methylcobalamin-dependent enzymatic reactions.

**Acknowledgment.** This research was funded by NIH Grant AN 18101. J.J.P. wishes to thank the Freshwater Foundation for financial support. We also wish to thank the reviewers' constructive comments and the suggestion of an alternative mechanism.

**Registry No.** $CH_3$-$B_{12}$, 13422-55-4; $H_2O$-$B_{12}^+$, 13422-52-1; $PtCl_6^{2-}$, 16871-54-8; $Pt(CN)_4Cl_2^{2-}$, 38725-65-4; $Pt(CN)_5Cl^{2-}$, 38725-82-5; $Pt(CN)_5I^{2-}$, 45000-44-0; $Pt(CN)_6^{2-}$, 41517-45-7; $PtCl_4^{2-}$, 13965-91-8; $Pt(CN)_4^{2-}$, 15004-88-3.

**Supplementary Material Available:** Plot to determine the formation constant of the trinuclear intermediate from absorbance changes at 630 nm for the demethylation by $Pt(CN)_5Cl^{2-}$/$Pt(CN)_4^{2-}$ (2 pages). Ordering information is given on any current masthead page.

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[25] For a recent review on the charge-transfer and electron-transfer reactions of organometallic compounds, see: Kochi, J. K. *Pure Appl. Chem.* 1980, *52*, 571.

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# Linking Molybdenum or Tungsten with Platinum. The Synthesis and Molecular Structure of PtMo($\mu$-$Ph_2Ppy$)($\mu$-CO)$(CO)_2Cl_2$ ($Ph_2Ppy$ = 2-(Diphenylphosphino)pyridine)

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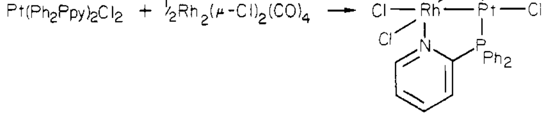
Reaction of $Pt(Ph_2Ppy)_2Cl_2$ ($Ph_2Ppy$ is 2-(diphenylphosphino)pyridine) with (bicycloheptadiene)$Mo(CO)_4$ or $(CH_3CN)_3W(CO)_3$ produces PtMo($\mu$-$Ph_2Ppy)_2$($\mu$-CO)$(CO)_2Cl_2$ (98% yield) or PtW($\mu$-$Ph_2Ppy)_2$($\mu$-CO)$(CO)_2Cl_2$ (67% yield), respectively. Infrared and $^{31}P\{^1H\}$ NMR spectra indicate that the Mo and W complexes have similar structures. PtMo($\mu$-$Ph_2Ppy)_2$($\mu$-CO)$(CO)_2Cl_2$ is also formed in the reaction between $Mo(Ph_2Ppy)_2(CO)_4$ (phosphorus-bound $Ph_2Ppy$) and (1,5-cyclooctadiene)$PtCl_2$. Red PtMo($\mu$-$Ph_2Ppy)_2$($\mu$-CO)$(CO)_2Cl_2$ crystallizes in the orthorhombic space group $I2cb$ ($\bar{c}ba$ of $Iba2$, No. 45) with $a$ = 13.784 (6) Å, $b$ = 17.677 (5) Å, $c$ = 31.915 (13) Å, $Z$ = 8, and $V$ = 7776.6 (5) Å$^3$. The structure was refined to a conventional $R$ value of 0.060 by using 3777 significant reflections and 232 parameters. The structure of the binuclear complex indicates that it possesses a Pt–Mo bond (2.845 (1) Å long) and a semibridging carbonyl group. Additional ligating atoms about Pt are 2P and Cl and about Mo are 2N, 2C (from CO), and Cl. The two bridging $Ph_2Ppy$ ligands assume a head-to-head arrangement with a trans-P–Pt–P unit and a cis-N–Mo–N unit.

## Introduction

In a recent series of articles,[1-7] we have shown that a variety of both homo- and heterobinuclear complexes that involve group 8 metal atoms can be synthesized by using 2-(diphenylphosphino)pyridine ($Ph_2Ppy$) as a bridging ligand. The strategy used in the synthesis of these compounds involves the initial binding of $Ph_2Ppy$ to one metal through a phosphorus atom. In a subsequent reaction with a second metal complex, the binuclear compound is formed. Examples of this latter step are shown in eq 1[1,6] and 2.[7] A common feature to all known reactions of this



(1)

type is the addition of one metal–halide bond to the second metal center. We believe that this behavior is a consequence of the rigid nature of the bridging ligand. This rigidity, in the case of a trans pair of bridging $Ph_2Ppy$ ligands, appears to limit the M–M separation to distances less than 2.7 Å.[2]

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[1] Farr, J. P.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* 1980, *101*, 6654.

[2] Farr, J. P.; Olmstead, M. M.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* 1981, *20*, 1182.

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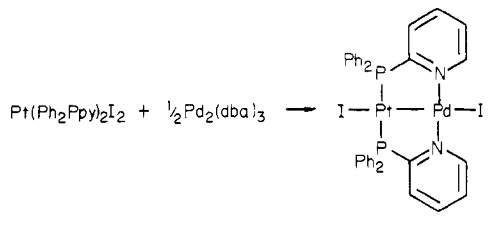
[7] Farr, J. P.; Wood, F. E.; Balch, A. L. *Inorg. Chem.*, in press.

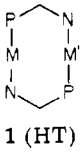
0276-7333/83/2302-1758$01.50/0



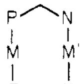
(2)

dba is dibenzylideneacetone

Another remarkable feature of these reactions is the mobility of the $Ph_2Ppy$ ligands. With two of these bridging ligands, three isomers (one head-to-tail (HT), 1, and two



1 (HT)



2 [HH (PM)]

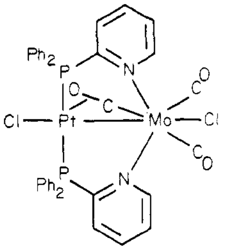
3 [HH (PM')]

head-to-head (HH), 2 and 3) are possible for a hetero binuclear complex. Examples of the formation of both HT (eq 1) and HH (eq 2) isomers are known. The formation of HT isomers from monomeric complexes involving P-bound $Ph_2Ppy$ requires rearrangement of the metal bonding to $Ph_2Ppy$. Similarly the thermal HH to HT isomerization, which has been observed for $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$[7] and $[RhPd(\mu\text{-}Ph_2Ppy)_2(CNCH_3)_2]^+$,[6] necessitates relocation of these bridging ligands.

Here we report on our first attempts to extend this chemistry so that a group 8 metal atom is connected to a second metal outside of group 8. This has resulted in the formation of molecules containing Pt–Mo and Pt–W bonds.

## Results and Discussion

**Synthetic Studies.** Reaction of $Pt(Ph_2Ppy)_2Cl_2$[5,7] with (bicycloheptadiene)molybdenum tetracarbonyl in dichloromethane at 38 °C for 18 h yields a red solution from which red crystals of $PtMo(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2$, 4, are obtained in nearly quantitative yield. The product has good solubility in dichloromethane and chloroform and is a nonelectrolyte in the first solvent. Its infrared spectrum in dichloromethane solution ($\nu$(CO) 1982, 1895, 1749 cm$^{-1}$) and as a solid suspended in Nujol ($\nu$(CO) 1961, 1874, 1740 cm$^{-1}$) indicates that two terminal and one bridging carbonyl environments are present. The $^{31}P\{^1H\}$ NMR spectrum of 4 in chloroform-*d* solution consists of a singlet at 34.4 ppm with the usual platinum satellites ($J$(Pt,P) = 3064 Hz). The magnitude of $J$(Pt,P) is consistent with the presence of phosphorus–platinum bonds trans to one another.[8] Further details of the structure of 4 come from the X-ray crystal structure analysis (vide infra).



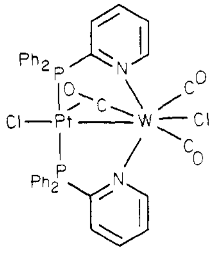
4

$PtMo(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2$ can also be obtained from a reaction in which the $Ph_2Ppy$ ligand is initially bound to molybdenum through phosphorus. The starting material in this case is $Mo(Ph_2Ppy)_2(CO)_4$, which was prepared by the reaction of the ligand with (bicycloheptadiene)molybdenum tetracarbonyl in dichloromethane solution.

Yellow $Mo(Ph_2Ppy)_2(CO)_4$ is moderately soluble in dichloromethane, and its $^{31}P\{^1H\}$ NMR spectrum in that solvent consists of a single resonance at 40.7 ppm which indicates that it is obtained as a single isomer. The high-frequency shift of the $^{31}P$ resonance relative to the free ligand is indicative of phosphorus coordination. We presume then that the nitrogen atoms remain uncoordinated. The infrared spectrum of $Mo(Ph_2Ppy)_2(CO)_4$ either in dichloromethane solution ($\nu$(CO) 2020, 1924 (sh), 1902, 1880 (sh) cm$^{-1}$) or in a Nujol mull ($\nu$(CO) 2020, 1930, 1882, 1834 cm$^{-1}$) indicates that it exists as the cis isomer. For comparison, *cis*-$Mo(PPh_3)_2(CO)_4$ has $\nu$(CO) at 2023, 1927, 1908, and 1897 cm$^{-1}$ in tetrachloroethylene solution.[9]

The reaction between *cis*-$Mo(Ph_2Ppy)_2(CO)_4$ and (1,5-cyclooctadiene)$PtCl_2$ proceeds readily in boiling dichloromethane to give $PtMo(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2$ in 76% yield. This reaction proceeds more rapidly than does the first synthesis, but its yield is lower. The spectroscopic properties of the products obtained by the two routes are identical.

$Pt(Ph_2Ppy)_2Cl_2$ also reacts with $W(NCCH_3)_3(CO)_3$ in boiling dichloromethane solution over an 18-h period to produce a red solution from which $PtW(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2$, 5, may be isolated in 67% yield. The spectroscopic properties of 5 are extremely similar to those of its molybdenum analogue 4, and, consequently, similar structural features are present. The $^{31}P\{^1H\}$ NMR spectrum, at 20 °C in chloroform-$d_1$ solution, consists of a single line at 34.3 ppm with flanking $^{195}Pt$ satellites which give $^1J$(Pt,P) of 3139 Hz. The infrared spectra of 5 show carbonyl stretching absorptions at 1974, 1885, and 1751 cm$^{-1}$ in dichloromethane solution and 1962, 1871, and 1772 cm$^{-1}$ in a Nujol mull.



5

**X-ray Crystallographic Structure of $PtMo(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2\cdot 0.406CH_2Cl_2$.** This material crystallizes with one molecule of the complex and one disordered molecule of dichloromethane in the asymmetric unit and no unusual intermolecular contacts. A perspective drawing of the complex molecule is shown in Figure 1. This figure also indicates the numbering scheme used to denote individual atoms. Final atomic positional parameters and thermal parameters are given in Table I. Table II contains selected interatomic distances, and Table III gives certain relevant interatomic angles. The crystal lattice imposes no symmetry upon the molecule. However, it has approximate $C_s$ symmetry with an effective mirror plane passing through the two metal atoms and the bridging carbonyl group.

At platinum the two phosphorus atoms, the chloride ligand, and the molybdenum atom lie in a plane with the platinum atom located at the center and displaced 0.18 Å

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Table I. Atom Coordinates (× $10^4$) and Temperature Factors (Å$^2$ × $10^3$) for PtMo($\mu$-Ph$_2$Ppy)$_2$($\mu$-CO)(CO)$_2$Cl$_2$

| atom | *x* | *y* | *z* | *U* |
|---|---|---|---|---|
| Pt | 2000 | 2393 (1) | 984 (1) | 18 (1)[a] |
| Mo | 2463 (1) | 1909 (1) | 1810 (1) | 18 (1)[a] |
| P(1) | 952 (4) | 1435 (3) | 982 (1) | 19 (1)[a] |
| P(2) | 2960 (3) | 3449 (3) | 1150 (1) | 22 (1)[a] |
| O(1) | 2706 (10) | 150 (7) | 1795 (4) | 30 (3) |
| O(2) | 4688 (10) | 1981 (8) | 2004 (4) | 31 (3) |
| O(3) | 3722 (11) | 1400 (8) | 1065 (4) | 31 (3) |
| Cl(1) | 2392 (4) | 1719 (3) | 2593 (1) | 30 (1)[a] |
| Cl(2) | 1487 (4) | 2903 (3) | 350 (1) | 30 (1)[a] |
| Cl(3) | 4557 (10) | 5206 (7) | 2339 (4) | 40 |
| Cl(4) | 4797 (11) | 5830 (8) | 1586 (4) | 40 |
| N(1) | 802 (12) | 1779 (9) | 1808 (4) | 25 (3) |
| N(2) | 2269 (9) | 3184 (7) | 1953 (4) | 15 (3) |
| C(1) | 309 (15) | 1528 (10) | 1464 (6) | 26 (4) |
| C(2) | −742 (16) | 1366 (11) | 1491 (6) | 35 (5) |
| C(3) | −1217 (18) | 1472 (12) | 1860 (6) | 42 (5) |
| C(4) | −717 (16) | 1733 (12) | 2214 (7) | 36 (5) |
| C(5) | 260 (15) | 1887 (10) | 2165 (6) | 28 (4) |
| C(6) | 1344 (13) | 462 (10) | 962 (5) | 19 (4) |
| C(7) | 2151 (15) | 258 (10) | 707 (5) | 31 (4) |
| C(8) | 2433 (18) | −458 (11) | 678 (6) | 37 (4) |
| C(9) | 1929 (22) | −1051 (13) | 882 (7) | 50 (6) |
| C(10) | 1098 (16) | −882 (12) | 1115 (6) | 34 (4) |
| C(11) | 829 (14) | −135 (11) | 1154 (6) | 29 (4) |
| C(12) | 6 (13) | 1525 (10) | 578 (5) | 20 (3) |
| C(13) | −630 (14) | 2117 (11) | 597 (6) | 27 (4) |
| C(14) | −1320 (16) | 2203 (12) | 296 (6) | 35 (4) |
| C(15) | −1313 (14) | 1739 (10) | −68 (6) | 26 (4) |
| C(16) | −643 (14) | 1171 (10) | −81 (6) | 29 (4) |
| C(17) | 6 (14) | 1058 (10) | 230 (5) | 23 (4) |
| C(18) | 2538 (15) | 3752 (9) | 1685 (5) | 23 (3) |
| C(19) | 2537 (17) | 4506 (11) | 1792 (5) | 31 (4) |
| C(20) | 2174 (13) | 4720 (10) | 2175 (5) | 28 (4) |
| C(21) | 1860 (14) | 4167 (10) | 2439 (5) | 29 (4) |
| C(22) | 1962 (18) | 3414 (10) | 2315 (6) | 34 (4) |
| C(23) | 2805 (14) | 4311 (10) | 846 (5) | 25 (4) |
| C(24) | 1860 (16) | 4570 (11) | 744 (6) | 39 (5) |
| C(25) | 1741 (15) | 5239 (11) | 528 (6) | 33 (5) |
| C(26) | 2539 (18) | 5648 (11) | 393 (6) | 38 (4) |
| C(27) | 3455 (19) | 5425 (13) | 472 (7) | 43 (5) |
| C(28) | 3670 (16) | 4745 (11) | 709 (6) | 36 (5) |
| C(29) | 4262 (14) | 3337 (10) | 1182 (5) | 24 (4) |
| C(30) | 4804 (16) | 3670 (12) | 1504 (6) | 33 (5) |
| C(31) | 5834 (17) | 3514 (12) | 1502 (6) | 39 (5) |
| C(32) | 6284 (19) | 3188 (14) | 1179 (7) | 47 (6) |
| C(33) | 5723 (17) | 2915 (13) | 838 (7) | 38 (5) |
| C(34) | 4738 (15) | 2981 (11) | 839 (6) | 29 (4) |
| C(35) | 2572 (16) | 809 (10) | 1804 (5) | 27 (4) |
| C(36) | 3824 (15) | 1967 (11) | 1912 (6) | 29 (4) |
| C(37) | 3130 (13) | 1684 (10) | 1285 (5) | 21 (4) |
| C(38) | 4625 (42) | 6160 (31) | 2002 (17) | 40 |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

from the plane toward the bridging carbonyl group. The two phosphorus atoms are trans to each other. The P(1)–Pt–P(2) angle is 166.1 (2)°, and the Cl(1)–Pt–Mo angle is 172.5 (1)°. The Pt–P distances are within the normal limits found for trans-P–Pt–P units. The Pt–Cl(2) distance (2.234 (4) Å) is in the normal range found for Pt–Cl distances and does not fall into the group of elongated M–Cl distances that are frequently found for cases where M–Cl is trans to a metal–metal bond.[6]

The Pt–Mo distance (2.845 (1) Å) is indicative of the presence of a Pt–Mo bond and is similar in length to the few other Pt–Mo bonds that are known. For comparison, the unbridged Pt–Mo distance in *trans*-Pt(CNC$_6$H$_{11}$)(C$_6$H$_{11}$NHCOC$_2$H$_5$){Mo(CO)$_3$($\eta^5$-C$_5$H$_5$)}$_2$ is 2.889 (2) Å,[10] and in Pt$_2$Mo$_2$($\eta^5$-C$_5$H$_5$)(CO)$_6$(PEt$_3$)$_2$[11] the two nonequivalent, carbonyl-bridged Pt–Mo bonds are 2.777 (1) and 2.835 (2) Å long (or 2.793 (1) and 2.846 (1) Å, depending on which of the two crystallographicaally distinct molecules is chosen).

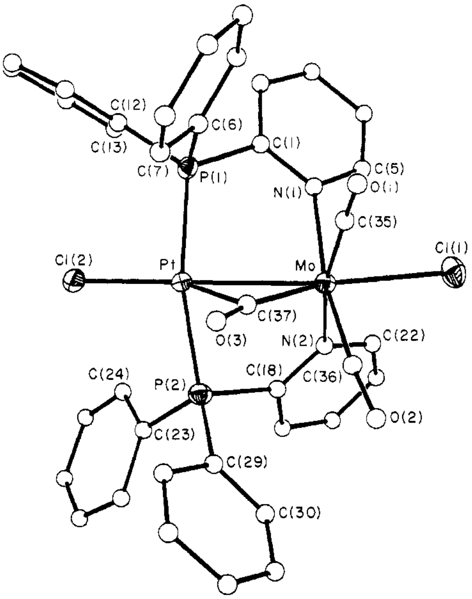

**Figure 1.** A perspective drawing of the structure of PtMo($\mu$-Ph$_2$Ppy)$_2$($\mu$-CO)(CO)$_2$Cl$_2$.

Table II. Selected Bond Lengths, Å, for PtMo($\mu$-Ph$_2$Ppy)$_2$($\mu$-CO)(CO)$_2$Cl$_2$

| | | | |
|---|---|---|---|
| | At Platinum | | |
| Pt-Mo | 2.845 (1) | Pt-P(1) | 2.227 (5) |
| Pt-P(2) | 2.348 (5) | Pt-Cl(2) | 2.324 (4) |
| Pt-C(37) | 2.218 (17) | | |
| | At Phosphorus | | |
| P(1)-C(1) | 1.783 (19) | P(2)-C(23) | 1.820 (18) |
| P(1)-C(12) | 1.841 (18) | P(2)-C(18) | 1.882 (17) |
| P(1)-C(6) | 1.803 (18) | P(2)-C(29) | 1.809 (19) |
| | At Molybdenum | | |
| Pt-Mo | 2.845 (1) | Mo-Cl(1) | 2.521 (4) |
| Mo-N(1) | 2.301 (17) | Mo-N(2) | 2.315 (12) |
| Mo-C(35) | 1.950 (18) | Mo-C(36) | 1.907 (20) |
| Mo-C(37) | 1.954 (17) | | |
| | Carbonyl Groups | | |
| O(1)-C(35) | 1.181 (22) | O(3)-C(37) | 1.187 (23) |
| O(2)-C(36) | 1.227 (24) | | |

The molybdenum atom is seven-coordinate. In addition to the bridging carbonyl group, it is bound to two terminal carbonyl groups, a terminal chloride ligand, two pyridine nitrogen atoms, and the platinum atom. The N$_2$C$_2$Cl group forms a nearly regular square pyramid with the molybdenum atom displaced 0.15 Å from the N$_2$C$_2$ plane, away from the chloride. The two pyridine nitrogen atoms are cis to each other (the N(1)–Mo–N(2) angle is 89.0 (5)°) and the two carbonyl groups are also cis (the C(35)–Mo–C(36) angle is 88.8 (8)°). The angles between the chloride and the four adjacent ligands lie in a narrow range, 82.9–87.2°, near the Cartesian ideal. The Mo–N and Mo–C distances are normal for molecules like MoBr(CO)$_2$($\eta^3$-C$_4$Ph$_3$O)(bpy) and MoBr(CO)$_2$($\eta^3$-C$_3$Ph$_3$)(bpy) which possess similar environments.[12] The Mo–Cl(1) distance of 2.521 (4) Å is

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(11) Bender, R.; Braunstein, P.; Dunusoy, Y.; Protas, J. *J. Organomet. Chem.* **1979**, *172*, C51.

(12) Drew, M. G. B.; Brisdon, B. J.; Day, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1310.

(13) Vahrenkamp, H. *Ber. Dtsch. Chem. Ges.* **1974**, *107*, 3867.

Table III. Selected Bond Angles, deg, for PtMo($\mu$-Ph$_2$Ppy)$_2$($\mu$-CO)(CO)$_2$Cl$_2$

| | | | | | |
|---|---|---|---|---|---|
| About Platinum | | | | | |
| Mo-Pt-P(1) | 85.3 (1) | P(2)-Pt-C(37) | 87.5 (5) | P(2)-Pt-Cl(2) | 93.4 (2) |
| P(1)-Pt-P(2) | 166.1 (2) | Mo-Pt-P(2) | 84.5 (1) | P(1)-Pt-C(37) | 91.5 (5) |
| P(1)-Pt-Cl(2) | 95.5 (2) | Mo-Pt-Cl(2) | 172.5 (1) | Cl(2)-Pt-C(37) | 144.0 (5) |
| Mo-Pt-C(37) | 43.2 (4) | | | | |
| About Phosphorus | | | | | |
| Pt-P(1)-C(1) | 104.5 (6) | Pt-P(1)-C(12) | 113.2 (6) | C(18)-P(2)-C(29) | 106.7 (8) |
| C(1)-P(1)-C(6) | 105.6 (8) | C(6)-P(1)-C(12) | 105.6 (8) | Pt-P(2)-C(23) | 118.6 (6) |
| C(1)-P(1)-C(12) | 104.2 (9) | Pt-P(2)-C(18) | 104.9 (6) | Pt-P(2)-C(29) | 119.0 (6) |
| Pt-P(1)-C(6) | 122.1 (6) | C(18)-P(2)-C(23) | 102.1 (8) | C(23)-P(2)-C(29) | 103.8 (9) |
| About Carbonyl Carbon | | | | | |
| Mo-C(35)-O(1) | 175.3 (18) | Mo-C(37)-O(3) | 156.5 (15) | Pt-C(37)-Mo | 85.7 (7) |
| Mo-C(36)-O(2) | 175.6 (15) | Pt-C(37)-O(3) | 117.7 (13) | | |
| About Molybdenum | | | | | |
| Pt-Mo-Cl(1) | 161.7 (1) | C(35)-Mo-C(36) | 88.8 (8) | Cl(1)-Mo-C(35) | 83.2 (5) |
| Cl(1)-Mo-N(1) | 87.2 (4) | Cl(1)-Mo-C(37) | 147.3 (5) | N(2)-Mo-C(35) | 169.0 (6) |
| Cl(1)-Mo-N(2) | 86.0 (3) | N(2)-Mo-C(37) | 115.0 (6) | Cl(1)-Mo-C(36) | 82.9 (6) |
| Pt-Mo-C(35) | 107.9 (5) | C(36)-Mo-C(37) | 72.2 (8) | N(2)-Mo-C(36) | 91.6 (6) |
| N(1)-Mo-C(35) | 88.7 (7) | Pt-Mo-N(1) | 78.7 (4) | Pt-Mo-C(37) | 51.0 (5) |
| Pt-Mo-C(36) | 111.3 (6) | Pt-Mo-N(2) | 82.2 (3) | N(1)-Mo-C(37) | 116.4 (6) |
| N(1)-Mo-C(36) | 170.0 (7) | N(1)-Mo-N(2) | 89.0 (5) | C(35)-Mo-C(37) | 75.6 (7) |
| About Nitrogen | | | | | |
| Mo-N(1)-C(1) | 122.1 (12) | Mo-N(2)-C(22) | 121.3 (11) | Mo-N(2)-C(18) | 124.0 (10) |
| C(1)-N(1)-C(5) | 116.1 (16) | Mo-N(1)-C(5) | 121.6 (12) | C(18)-N(2)-C(22) | 114.5 (14) |

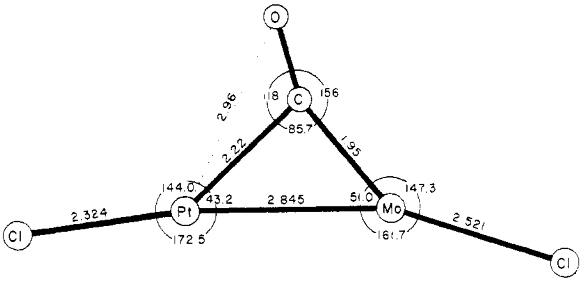

**Figure 2.** The planar portion of the structure of PtMo($\mu$-Ph$_2$Ppy)$_2$($\mu$-CO)(CO)$_2$Cl$_2$ showing the semibridging carbonyl group.

somewhat long for terminal Mo–Cl bonds and probably suffers from the trans effect of the platinum and bridging carbonyl group.

The unique carbonyl group responsible for the low-energy carbonyl absorption in the infrared spectrum resides in a semibridging environment. This is best discussed in the context of Figure 2, which shows a nearly planar group of atoms which includes Pt, Mo, Cl(1), Cl(2), C(37), and O(3). The semibridging carbonyl group is more closely associated with the molybdenum atom than it is with the platinum atom, and the O(3)–C(37)–Mo angle (156°) is not too far distorted from linearity.

We suspect that the semibridging carbonyl ligand falls into the class of semibridging carbonyls which result primarily from intramolecular crowding. The platinum atom would appear to have little intrinsic need to bond to an additional ligand. In complexes such as PtRh($\mu$-Ph$_2$Ppy)$_2$(CO)Cl$_3$,[5] PdRh($\mu$-Ph$_2$Ppy)$_2$(CO)Cl$_3$,[1,6] and PdRu($\mu$-Ph$_2$Ppy)$_2$(CO)$_2$Cl$_2$,[4] which have similarly situated platinum or palladium atoms (each with a 16-electron count), there is no evidence for interactions with the available carbonyl groups. A major difference between these complexes and PtMo($\mu$-Ph$_2$Ppy)$_2$($\mu$-CO)(CO)$_2$Cl$_2$ and its tungsten analogue is the coordination number of the second metal atom. In the latter two complexes (**4** and **5**), the molybdenum and tungsten atoms are seven-coordinate while in the preceding group, the rhodium and ruthenium atoms are only six-coordinate. Thus, crowding may force one carbonyl group in **4** and **5** to lie over the platinum atom, and in that position it is likely to be acting as a weak $\pi$-donor toward the somewhat electron-deficient, 16-electron, platinum atom.

The bridging Ph$_2$Ppy ligands are in a head-to-head arrangement as the $^{31}$P NMR spectra showed. They are aligned so that the two phosphorus atoms, which are bound to platinum, are trans to one another while the two nitrogen atoms, which are bound to molybdenum, are cis to each other. It appears that these bridging ligands are under strain which is produced by the relatively long Pt–Mo distance. In previous examples of bridging Ph$_2$Ppy ligands, the metal–metal separations have fallen in the limited range 2.660–2.594 Å.[1,2,4,6] We have commented previously that this ligand may have difficulty in accommodating longer metal–metal separations and have ascribed the reduced reactivity of metal–metal bonds in complexes with Ph$_2$Ppy bridges to the constraints of the bridging group.[2,3] In the present example, the trans (Pt)/cis (Mo) arrangement (in contrast to a hypothetical trans (Pt)/trans (Mo) arrangement) undoubtedly helps to span the long Pt–Mo distance. Additionally this arrangement allows the carbonyl ligands to lie trans to the pyridine ligands rather than trans to one another where they would compete as $\pi$-acceptors for one metal $d_\pi$ orbital. This is, however, not the first example of such an arrangement; PdRu($\mu$-Ph$_2$Ppy)$_2$(CO)$_2$Cl$_2$ has a trans (Pd)/cis (Ru) orientation but in this case as an HT isomer.

The Pt/Mo (or W) reactions described here continue the pattern in which Ph$_2$Ppy facilitates the oxidative addition of a metal halogen bond to a second metal center. The products, PtMo($\mu$-Ph$_2$Ppy)$_2$($\mu$-CO)(CO)$_2$Cl$_2$ and PtW($\mu$-Ph$_2$Ppy)$_2$($\mu$-CO)(CO)$_2$Cl$_2$, each contain a seven-coordinate, 18-electron molybdenum or tungsten center bound to a 16-electron (or 18-electron, if the semibridging carbonyl donates two electrons) platinum atom. This procedure represents a new means of generating Pt–Mo and Pt–W bonds. Previous examples have involved metathesis of a Pt–Cl unit with C$_5$H$_5$Mo(CO)$_3^-$ [10,11] and the Stone reaction, in which a platinum(0) compound is added to carbene or

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Table IV. Summary of Crystal Data, Data Collection, and Refinement

| | |
|---|---|
| formula | $PtMoCl_2P_2N_2O_3C_{37}H_{28}\cdot CH_2Cl_2$ |
| fw | 1057.46 |
| space group | *I2cb* ($\bar{c}ba$ of *Iba*2, No. 45) |
| *a*, Å | 13.784 (6) |
| *b*, Å | 17.677 (5) |
| *c*, Å | 31.915 (13) |
| *V*, Å$^3$ | 7776.6 (5) |
| *Z* | 8 |
| $d_{calcd}$, g/cm$^3$ | 1.81 (140 K) |
| $d_{exptl}$, g/cm$^3$ | 1.77 (298 K) |
| cryst dimens, mm | 0.125 × 0.25 × 0.45 |
| radiation | Mo K$\alpha$ (graphite monochromator), $\lambda$ = 0.710 69 Å |
| temp, K | 140 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 42.0 |
| range abs corr fac | 2.3-3.1 |
| scan method | $\omega$ |
| $2\theta$ max, deg | 50 |
| diffractometer | $P2_1$ |
| octant collected | $+h, +k, +l$ |
| no. of refl measd | 3782 |
| no. of unique data | 3777 |
| no. of data with $I > 3\sigma(I)$ | 3200 |
| *R* | 0.060 |
| $R_w$ | 0.064 |
| no. of parameters refined | 232 |
| mean shift/esd last cycle | 0.019 |

carbyne compound of molybdenum or tungsten.[15,16]

The formation of the HH (P,Pt) isomers in these reactions is clearly, in the case of 4, due to the thermodynamic stability of this arrangement. The fact that only one isomer is formed, regardless of whether the $Ph_2Ppy$ is initially bound through phosphorus to platinum or molybdenum, indicates that kinetic control of the product is not operating.

Studies of the chemical reactivity of these unusual binuclear species are in progress.

## Experimental Section

**Synthesis of Compounds.** 2-(Diphenylphosphino)pyridine,[4] $Pt(Ph_2Ppy)_2Cl_2$,[5] $W(CO)_3(CH_3CN)_3$,[17] $(C_7H_8)Mo(CO)_4$[18] and Pt(COD)$Cl_2$ were obtained by routes described elsewhere.

**MoPt($\mu$-Ph$_2$Ppy)$_2$($\mu$-CO)(CO)$_2$Cl$_2$. Method 1.** A solution of 205 mg (0.700 mmol) of (bicycloheptadiene)molybdenum tetracarbonyl and 575 mg (0.700 mmol) of $Pt(Ph_2Ppy)_2Cl_2$ in 40 mL of dichloromethane was heated under reflux for 18 h. After the solution was cooled, 10 mL of absolute ethanol was added to it. The dichloromethane was evaporated by using a rotary evaporator. The red crystals that precipitated in the ethanol were collected by filtration, washed with absolute ethanol and ethyl ether, and vacuum dried; yield 694 mg (98%). Anal. Calcd for $C_{37}H_{28}Cl_2MoN_2O_3P_2Pt$: C, 45.70; H, 2.90; N, 2.90. Found: C, 44.25; H, 3.01; N, 2.67.

**Method 2.** A solution of 390 mg (0.530 mmol) of Mo$(Ph_2Ppy)_2(CO)_4$ and 200 mg (0.530 mmol) of Pt(COD)$Cl_2$ in 40 mL of dichloromethane was heated under reflux for 3 h. After the solution was cooled, 10 mL of absolute ethanol was added to it. The dichloromethane was evaporated by using a rotary evaporator. The red crystals that precipitated in the ethanol were collected by filtration, washed with absolute ethanol and ethyl ether, and vacuum dried; yield 360 mg (74%). The physical properties of the product were identical with those obtained from material prepared by the preceding route.

***cis*-Mo(Ph$_2$Ppy)$_2$(CO)$_4$.** A solution of 400 mg (1.33 mmol) of (bicycloheptadiene)molybdenum tetracarbonyl and 650 mg (2.46 mmol) of 2-(diphenylphosphino)pyridine in 20 mL of dichloromethane was stirred for 30 min. The yellow crystalline solid that formed was collected by filtration, washed with ethyl ether, and vacuum dried; yield 296 mg (71%). Anal. Calcd for $C_{38}H_{28}MoN_2O_4P_2$: C, 62.14; H, 3.84; N, 3.81. Found: C, 61.85; H, 3.62; N, 3.66.

**PtW($\mu$-Ph$_2$Ppy)($\mu$-CO)(CO)$_2$Cl$_2$.** A solution of 481 mg (0.600 mmol) of $Pt(Ph_2Ppy)_2Cl_2$ and 250 mg (0.600 mmol) of $W(CO)_3(CH_3CN)_3$ in 40 mL of a 1:1 dichloromethane-acetone mixture was heated under reflux for 18 h. After the solution had cooled, 10 mL of absolute ethanol was added to it. The dichloromethane was evaporated by using a rotary evaporator. The red crystals that precipitated in the ethanol were collected by filtration, washed with absolute ethanol and ethyl ether, and vacuum dried; yield 458 mg (67%). Anal. Calcd for $C_{37}H_{28}N_2O_3Cl_2P_2WPt$: C, 41.90; H, 2.66; N, 2.64. Found: C, 41.09; H, 2.76; N, 2.56.

**X-ray Crystallography.** Red, prismatic crystals of PtMo($\mu$-Ph$_2$Ppy)$_2$($\mu$-CO)(CO)$_2$Cl$_2\cdot$0.406CH$_2$Cl$_2$ were obtained from slow evaporation of a dichloromethane solution. Crystal data, data collection procedure, and refinement of the structure are summarized in Table IV.[19] The lattice was found to be orthorhombic *I* by standard procedures using the $P2_1$ software. Using fast scans, the conditions $hkl$, $h + k + l = 2n$, $hk0$, $h = 2n$ ($k = 2n$), $h0l$, $h = 2n$ ($l = 2n$) were observed. The possible space groups were *I2cb* ($\bar{c}ba$ of *Iba*2, No. 45) and *Imcb* ($\bar{c}ba$ of *Ibam*, No. 72). On the basis of the Patterson map and the distribution of $|E^2 - 1|$, the noncentrosymmetric space group *I2cb* was selected. The structure was solved by locating the Pt and Mo positions using the Patterson map. The successful solution of the structure in this space group confirms its choice. Enantiomer determination was carried out in two ways: by refining to ±1 a variable which multiplies all $\Delta f''$ values and by application of the program ABSCON.[20] Both methods indicated the original choice of hand was incorrect, and refinement was continued with all *y* coordinates inverted. Final blocked-cascade least-squares refinement was carried out with Pt, Mo, Cl(1), Cl(2), and P atoms anisotropic, the remaining non-hydrogen atoms isotropic, hydrogen atoms at calculated positions that were recalculated with each cycle ($U_{iso}$ fixed at 1.2 times the $U_{iso}$ for the bonded carbon atom), and a variable occupancy for a disordered molecule of dichloromethane. The latter parameter refined to a value of 0.406 with $U_{iso}$ of Cl(3), Cl(4), and C(38) fixed at 0.04 Å$^2$. The largest feature in a final difference map was 3.7 e Å$^{-3}$ near Pt; other smaller features are near Pt, Mo, and $CH_2Cl_2$. The largest shift/esd in the final cycle of refinement was 0.114 for overall scale. A table of final atomic coordinates is presented in Table I.

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**Registry No.** 4, 87262-98-4; 5, 87262-99-5; *cis*-Mo$(Ph_2Ppy)_2(CO)_4$, 87263-00-1; Pt, 7440-06-4; Mo, 7639-98-7; W, 7440-33-7.

**Supplementary Material Available:** Tables of calculated hydrogen coordinates, anisotropic thermal parameters, structure factors, and least-squares planes and a complete list of bond distances and angles (22 pages). Ordering information is given on any current masthead page.

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