916 *Inorg. Chem.* **1996,** *35,* 916−922

Synthesis and Electrochemistry of Heterobimetallic Ruthenium/Platinum and Molybdenum/Platinum Complexes

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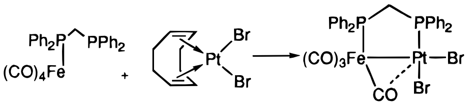
Received August 23, 1995⊗

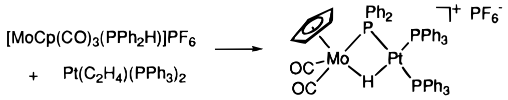
As starting materials for heterobimetallic complexes, $[RuCp(PPh_3)CO(PPh_2H)]PF_6$ and $[RuCp(PPh_3)CO(\eta^1\text{-dppm})]PF_6$ were prepared from $RuCp(PPh_3)(CO)Cl$. In the course of preparing $[RuCp(\eta^2\text{-dppm})(\eta^1\text{-dppm})]Cl$ from $RuCp(Ph_3P)(\eta^1\text{-dppm})Cl$, the new monomer $RuCpCl(\eta^1\text{-dppm})_2$ was isolated. The uncommon coordination mode of the two monodentate bis(phosphines) was confirmed by X-ray crystallography [$a = 11.490(1)$ Å, $b = 14.869(2)$ Å, $c = 15.447(2)$ Å, $\alpha = 84.63(1)°$, $\beta = 70.55(1)°$, $\gamma = 72.92(1)°$, $V = 2378.7(5)$ Å^3, $d_{calc} = 1.355$ g cm^{-3} (298 K), triclinic, $P\bar{1}$, $Z = 2$]. The dppm-bridged bimetallic complexes $RuCp(PPh_3)Cl(\mu\text{-dppm})PtCl_2$, $RuCpCl(\mu\text{-dppm})_2PtCl_2$, and $[RuCp(PPh_3)CO(\mu\text{-dppm})PtCl_2]PF_6$ each exhibit electrochemistry consistent with varying degrees of metal−metal interaction. The cationic heterobimetallic complexes $[Mo(CO)_3(\mu\text{-dppm})_2Pt(H)]PF_6$ and $[MoCp(CO)_2(\mu\text{-PPh}_2)(\mu\text{-H})Pt(PPh_3)(MeCN)]PF_6$ were prepared by chloride abstraction from the corresponding neutral bimetallic species and show electrochemical behavior similar to the analogous Ru/Pt complexes.

Introduction

Interest in bimetallic compounds as models for surface and catalytic reactions has led to extensive research in this area.[1,2] Heterobinuclear complexes are of particular interest since the differing reactivities of the metals may be exploited in chemical transformations.[3,4] However, it is often difficult to determine whether observed reactivity is due to the bimetallic complex itself or to monometallic complexes formed upon fragmentation of the starting complexes under the reaction conditions.[3] In order to address this problem, various synthetic strategies have been employed to ensure the integrity of the bimetallic structure. One of the most successful of these utilizes bridging ligands, commonly bidentate phosphines such as dppm[5−9] or μ-phosphido[3,10] moieties. A representative example of this approach is shown in eq 1.[8a] The monomeric iron complex is constructed with the pendant dppm attached. The second metal is then added as an unsaturated fragment generated *in situ* by loss of the labile COD ligand. Another common approach to heterobinuclear compounds uses "bridge-assisted synthesis"[2,6] in preparing μ-phosphido ligands (eq 2).[10a] In this strategy, a metal with a coordinated secondary phosphine is deprotonated, and the resulting terminal phosphido ligand displaces a labile ligand from the second metal affording the μ-phosphido-bridged dimer.



(1)



(2)

Our interest in methanol oxidation at platinum electrodes bearing either molybdenum or ruthenium atoms[11] has led us to investigate the properties of Mo/Pt and Ru/Pt bimetallic complexes. Although heterobinuclear complexes are common in the literature, the number of Ru/Pt complexes is rather small

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⊗ Abstract published in *Advance ACS Abstracts,* January 15, 1996.

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(5) Abbreviations: dppm = bis(diphenylphosphino)methane, dppe = bis(diphenylphosphino)ethane, Cp = cyclopentadienyl, TBAH = tetrabutylammonium hexafluorophosphate, COD = 1,5-cyclooctadiene, DME = dimethoxyethane.

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0020-1669/96/1335-0916$12.00/0

(Mo/Pt complexes are more common). The electrochemical properties of these compounds, for the most part, remain uninvestigated. We report here the synthesis, structure, and electrochemical characterization of some new Mo/Pt and Ru/Pt heterobinuclear complexes with bis(phosphine) and phosphido bridges. The focus of the work is characterization of the dimeric species using cyclic voltammetry and correlation of the observed redox potentials with those of the analogous monomers to gain insight into the oxidation behavior of the binuclear complexes.

Experimental Section

General Methods. Standard Schlenk/vacuum techniques were used throughout. Hexane, petroleum ether, chloroform, and methylene chloride were distilled from CaH_2. Diethyl ether, THF, toluene, and dimethoxyethane were distilled from Na/Ph_2CO. All NMR solvents were degassed by three freeze−pump−thaw cycles. Benzene-d_6 was vacuum transferred from Na/Ph_2CO. $CDCl_3$ was stored over 3 Å molecular sieves. All other starting materials were purchased in reagent grade and used without further purification. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on Varian VXR-300 or Gemini-300 NMR spectrometers. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. Elemental analyses were performed at the University of Florida.

Electrochemical experiments were performed under nitrogen using a PAR Model 273 potentiostat/galvanostat or an IBM EC225 voltammetric analyzer. Cyclic voltammograms were recorded at room temperature in a standard three-electrode cell with a glassy carbon working electrode. All potentials are reported vs NHE and were determined in CH_2Cl_2 or dimethoxyethane (DME) using 0.5 or 0.1 M TBAH, respectively. Ferrocene ($E_{1/2} = 0.55$ V), decamethylferrocene ($E_{1/2} = 0.04$ V), or cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) was used *in situ* as a calibration standard. Bulk electrolyses were performed using 2.0 × 3.5 cm stainless steel plates for the working and auxiliary electrodes in a standard three-electrode cell. The stirred solutions were electrolyzed at the appropriate potential until a color change was observed. $RuCp(Ph_3P)(CO)Cl$,[12] $RuCp(Ph_3P)(\eta^1\text{-dppm})Cl$,[13] $Pt(COD)Cl_2$,[14] $Pt(PhCN)_2Cl_2$,[15] $Mo(CO)_3(\mu\text{-dppm})_2Pt(H)Cl$,[16] and $MoCp(CO)_2(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)Cl$[17] were prepared by literature methods. $Ru_3(CO)_{12}$, K_2PtCl_4, $PtCl_2$, and $RuCl_3\cdot xH_2O$ were obtained from Johnson Matthey and used as received.

Preparation of $[RuCp(PPh_3)CO(PPh_2H)]PF_6$ (1). $RuCp(PPh_3)(CO)Cl$ (0.5 g, 1 mmol) was added to a flask containing MeOH (20 mL) and PPh_2H (0.95 g, 5.1 mmol, 0.88 mL). A solution of NH_4PF_6 (0.50 g, 3.1 mmol) in MeOH (15 mL) was added via cannula and the mixture heated to 60 °C for 12 h. After cooling to room temperature, the volatile components were removed *in vacuo* and CH_2Cl_2 (20 mL) was added to the residue giving a bright yellow solution and a white precipitate. The supernatant was filtered through Celite and concentrated to *ca.* 10 mL, and ether (15 mL) was added, resulting in the formation of a white microcrystalline solid over 1 h. After the mother liquor was removed via cannula, the solid was washed with ether, redissolved in a minimal amount of CH_2Cl_2, and reprecipitated with ether to give **1** as 0.49 g of a white solid (61% yield). Note: The product contained 0.5 equiv of CH_2Cl_2 as indicated by ^1H NMR. ^1H NMR ($CDCl_3$): δ 7.5−7.0 (m, 25H, PPh_3 and PPh_2H), 6.8 and 5.5 (1H, dd, J_{PH} = 384, 8 Hz, PPh_2H), 5.11 (s, 5H, *Cp*). ^{13}C NMR ($CDCl_3$): δ 200.2 (t, J_{CP} = 17 Hz, *C*O), 133.0 (d, J_{CP} = 11 Hz), 132.6 (d, J_{CP} = 11 Hz), 131.9 (s), 131.6 (d, J_{CP} = 2 Hz), 130.6 (d, J_{CP} = 19 Hz), 129.5 (d, J_{CP} = 19 Hz), 129.4 (d, J_{CP} = 20 Hz), 129.1 (d, J_{CP} = 11 Hz), 89.5 (s, *Cp*). ^{31}P NMR ($CDCl_3$): δ 48.1 (d, J_{PP} = 32 Hz, *P*Ph$_3$), 30.0 (d, J_{PP} = 32 Hz, *P*Ph$_2$H). IR (CH_2Cl_2): ν_{CO} = 1989 (s) cm^{-1}. CV (CH_2Cl_2): E_{pa} = 1.95 V. Anal. Calcd for $C_{36}H_{31}F_6OP_3Ru\cdot 0.5CH_2Cl_2$: C, 52.80; H, 3.86. Found: C, 53.24; H, 3.59.

Preparation of $[RuCp(PPh_3)CO(\eta^1\text{-dppm})]PF_6$ (2). $RuCp(PPh_3)(CO)Cl$ (0.5 g, 1 mmol), dppm (1.17 g, 3.05 mmol), and NH_4PF_6 (0.50 g, 3.1 mmol) were dissolved in MeOH (100 mL). The mixture was heated to 60 °C for 8 h and then allowed to cool to room temperature. The solvent was removed to give a bright yellow residue, CH_2Cl_2 (25 mL) was added, and the supernatant was filtered through Celite. The volatile components were removed to give a yellow solid that was washed with hexane (3 × 10 mL) and recrystallized twice from 2:5 CH_2Cl_2/ether to give 0.14 g of **2** as an off-white solid (14% yield). Note: The product contained 0.25 equiv of CH_2Cl_2 as indicated by ^1H NMR. ^1H NMR ($CDCl_3$): δ 7.8−6.9 (m, 35H, PPh_3 and $Ph_2P-CH_2-PPh_2$), 4.96 (s, 5H, *Cp*), 2.70 (br d, 1H, J_{HH} = 16 Hz, $Ph_2P-CH_2-PPh_2$), 1.79 (dd, 1H, J_{HH} = 16 Hz, J_{PH} = 10 Hz, $Ph_2P-CH_2-PPh_2$). ^{31}P NMR ($CDCl_3$): δ 44.9 (d, J_{PP} = 27 Hz, *P*Ph$_3$), 34.5 (dd, J_{PP} = 47, 27 Hz, Ru−*P*Ph$_2$−CH$_2$−PPh$_2$), −28.6 (d, J_{PP} = 47 Hz, Ru−PPh$_2$−CH$_2$−*P*Ph$_2$). IR (CH_2Cl_2): ν_{CO} = 1976 (s) cm^{-1}. CV (CH_2Cl_2): E_{pa} = 1.91 V. Anal. Calcd for $C_{49}H_{42}F_6OP_4Ru\cdot 0.25CH_2Cl_2$: C, 58.73; H, 4.22. Found: C, 58.85; H, 4.28.

Preparation of $RuCp(\eta^1\text{-dppm})_2Cl$ (3). In the course of preparing $[RuCp(\eta^2\text{-dppm})(\eta^1\text{-dppm})]Cl$ from $RuCp(Ph_3P)(\eta^1\text{-dppm})Cl$ (2.41 g, 2.84 mmol) and dppm (1.64 g, 4.26 mmol),[13] the orange mother liquor obtained after precipitation of this complex was evaporated to dryness to give an orange solid. The solid was redissolved in a minimal amount of CH_2Cl_2 (5 mL) and filtered through Celite. Hexane (15 mL) was added and the solution allowed to stand undisturbed over several hours, resulting in the formation of a red/orange crystalline solid. A second recrystallization of the resulting solid from CH_2Cl_2/hexane gave **3** as 0.92 g of red/orange crystals (33% yield). The remainder of the ruthenium from the reaction was identified as **3**, $RuCp(\eta^2\text{-dppm})Cl$,[18] and starting material (*vide infra*). Attempts to separate these complexes via further chromatography failed. **3.** ^1H NMR ($CDCl_3$): δ 7.3−6.8 (m, 40H, $Ph_2P-CH_2-PPh_2$), 4.39 (s, 5H, *Cp*), 3.70 (br d, 2H, J_{HH} = 15 Hz, $Ph_2P-CH_2-PPh_2$), 1.91 (br d, 2H, $Ph_2P-CH_2-PPh_2$). ^{13}C NMR ($CDCl_3$): δ 133.2 (d, J_{CP} = 56 Hz), 132.9 (d, J_{CP} = 55 Hz), 129.0 (d, J_{CP} = 9 Hz), 128.3 (d, J_{CP} = 22 Hz), 128.1 (d, J_{CP} = 30 Hz), 128.0 (d, J_{CP} = 2 Hz), 127.6 (m), 126.9 (m), 84.3 (s, *Cp*), 25.8 (m). ^{31}P NMR ($CDCl_3$): δ 39.3 (overlapping d of virtual t, J_{PP} = 41, 34 Hz, Ru−*P*Ph$_2$−CH$_2$−PPh$_2$), −25.2 (overlapping d of virtual t, J_{PP} = 41, 32 Hz, Ru−PPh$_2$−CH$_2$−*P*Ph$_2$). CV (CH_2Cl_2): $E_{1/2}$ = 0.50 V. Anal. Calcd for $C_{55}H_{49}ClP_4Ru$: C, 68.08; H, 5.09. Found: C, 68.19; H, 5.08.

Preparation of $RuCp(PPh_3)Cl(\mu\text{-dppm})PtCl_2$ (4). A Schlenk flask was charged with $RuCp(PPh_3)(\eta^1\text{-dppm})Cl$ (1.5 g, 1.8 mmol) and CH_2Cl_2 (50 mL). A solution of $Pt(COD)Cl_2$ (0.66 g, 1.8 mmol) in CH_2Cl_2 (25 mL) was then added via cannula to give a red/orange solution. The solution was stirred overnight at room temperature and filtered through Celite. Removal of solvent afforded a red/orange solid which was washed with 1:1 hexane/ether to give an orange/brown residue. The residue was dissolved in CH_2Cl_2 with gentle heating and reprecipitated with 1:1 hexane/ether, giving **4** as 1.51 g of an orange powder (77% yield). ^1H NMR ($CDCl_3$): δ 8.0−6.0 (m, 35H, $Ph_2P-CH_2-PPh_2$ and PPh_3), 4.59 (s, 5H, *Cp*), 2.71 (overlapping m, 2H, $Ph_2P-CH_2-PPh_2$). ^{13}C NMR (CD_2Cl_2): δ 137.9−127.2 (aromatic), 82.0 (s, *Cp*), 59.4 (m, $PPh_2-CH_2-PPh_2$). ^{31}P NMR ($CDCl_3$): δ 49.1 (dd, J_{PP} = 21, 36 Hz, Ru−*P*Ph$_2$−CH$_2$−PPh$_2$), 37.8 (d, J_{PP} = 36 Hz, Ru−*P*Ph$_3$), −2.9 (d, J_{PP} = 20 Hz, J_{PPt} = 3826 Hz, Ru−PPh$_2$−CH$_2$−*P*Ph$_2$). CV (CH_2Cl_2): $E_{1/2}$ = 1.13 V, E_{pa} = 1.78 V. Anal. Calcd for $C_{48}H_{42}Cl_3P_3PtRu$: C, 51.74; H, 3.80. Found: C, 51.32; H, 3.80.

Preparation of $RuCpCl(\mu\text{-dppm})_2PtCl_2$ (5). $RuCp(\eta^1\text{-dppm})_2Cl$ (**3**, 0.15 g, 0.16 mmol) was dissolved in 10 mL of CH_2Cl_2, and a solution of $Pt(PhCN)_2Cl_2$ (0.07 g, 0.16 mmol) in CH_2Cl_2 (5 mL) was added. After the mixture was stirred overnight, the solvent was removed,

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(18) See ref 13 for original report of the complex. Our spectral data for $RuCp(\eta^2\text{-dppm})Cl$ differ from those reported. The identity of the compound was confirmed with an X-ray crystal structure (Terry, M. R.; Abboud, K.; McElwee-White, L. Unpublished results.) ^1H NMR ($CDCl_3$): δ 7.7−7.2 (m, 20H, $Ph_2P-CH_2-PPh_2$), 5.06 (dt, 1H, J_{HH} = 14.7 Hz, J_{PH} = 10.2 Hz, $Ph_2P-CH_2-PPh_2$), 4.69 (s, 5H, *Cp*), 4.34 (dt, 1H, J_{HH} = 14.7 Hz, J_{PH} = 11.1 Hz, $Ph_2P-CH_2-PPh_2$). ^{31}P NMR ($CDCl_3$): δ 13.6 (s, *P*Ph$_2$−CH$_2$−*P*Ph$_2$).

affording an orange solid. The solid was reprecipitated from CH_2Cl_2/hexane to give **5** as 0.18 g of an orange powder (91% yield). Note: The product contained 1 equiv of CH_2Cl_2 as indicated by ^1H NMR. ^1H NMR ($CDCl_3$): δ 8.12 (m, 8H), 7.46−6.77 (aromatic, 32H), 5.03 (s, 5H, *Cp*), 3.21 (m, 4H, $Ph_2P-CH_2-PPh_2$). ^{13}C NMR ($CDCl_3$): δ 133.9−127.5 (aromatic), 91.3 (s, *Cp*), 61.8 (m, $Ph_2P-CH_2-PPh_2$). ^{31}P NMR ($CDCl_3$): δ 43.2 (d, $J_{PP} = 24$ Hz, $Ru-PPh-CH_2-PPh_2$), −2.6 (d, $J_{PP} = 19$ Hz, $J_{PPt} = 2372$ Hz, $PPh_2-CH_2-PhP-Pt$). CV (CH_2Cl_2): $E_{pa1} = 1.13$ V, $E_{pa2} = 1.45$ V. Anal. Calcd for $C_{55}H_{49}Cl_3P_4Pt$-$Ru{\cdot}CH_2Cl_2$: C, 50.90; H, 3.86. Found: C, 50.70; H, 3.78.

Preparation of [RuCp(PPh₃)CO(*μ*-dppm)Pt(Cl)₂]PF₆ (6). RuCp(PPh₃)Cl(*μ*-dppm)PtCl₂ (**4**, 0.143 g, 0.129 mmol) was partially dissolved in DME, and then CO was bubbled through the mixture for 15 min. A CO-saturated solution of $TlPF_6$ (0.055 g, 0.16 mmol) in DME was added and the mixture stirred under ambient CO pressure for 10 h. The mixture was filtered and the filtrate evaporated to dryness. Reprecipitation from DME and Et_2O gave **6** as 0.11 g of a yellow solid (73% yield). ^1H NMR ($CDCl_3$): δ 7.98 (m, 4H), 7.66−7.22 (aromatic, 31H), 5.59 (s, 5H, *Cp*), 2.17 (m, 2H, $Ph_2P-CH_2-PPh_2$). ^{13}C NMR ($CDCl_3$): δ 218.4 (s, *C*O), 133.0−132.2, 129.8−128.1 (aromatic), 90.7 (s, *Cp*), 71.8 (m, $Ph_2P-CH_2-PPh_2$). IR (CH_2Cl_2): $\nu_{CO} = 1979$ (s) cm^{-1}. CV (CH_2Cl_2): $E_{pa1} = 1.43$ V, $E_{pa2} = 1.68$ V. Anal. Calcd for $C_{49}H_{42}Cl_2F_6P_4PtRu$: C, 50.13; H, 3.58. Found: C, 49.81; H, 3.40.

Preparation of [Mo(CO)₃(*μ*-dppm)₂Pt(H)]PF₆ (7). Mo(CO)₃(*μ*-dppm)₂Pt(H)Cl (0.75 g, 0.64 mmol) was dissolved in CH_2Cl_2 (20 mL) and MeCN (10 mL). A slurry of $TlPF_6$ (0.22 g, 0.64 mmol) in CH_2Cl_2 (10 mL) was added, resulting in an orange/brown solution over an off-white precipitate. The mixture was stirred for 30 min and then filtered through Celite. Ether (15 mL) was added to the filtrate, giving a microcrystalline solid over 30 min. The product was recrystallized from CH_2Cl_2/ether and dried under vacuum to give **7** as 0.74 g of an orange microcrystalline solid (90% yield). Note: The product contained 1 equiv of CH_2Cl_2 as indicated by ^1H NMR. ^1H NMR (CD_2Cl_2): δ 7.5−7.1 (m, 40H, $Ph_2P-CH_2-PPh_2$), 3.12 (br m, 4H, $Ph_2P-CH_2-PPh_2$), −2.86 (tt, $J_{HPt} = 1453$ Hz, $J_{HP} = 11$ Hz, $Pt-H$). ^{13}C NMR ($CDCl_3$): δ 232.1, 191.6, 190.8 (*C*O), 149.3, 135.1−128.3 ($Ph_2P-CH_2-PPh_2$), 66.2 ($Ph_2P-CH_2-PPh_2$). ^{31}P NMR (CD_2Cl_2): δ 42.9 (t, $J_{PP} = 46$ Hz, $Mo-Ph_2P-CH_2-PPh_2$), 22.1 (d, $J_{PP} = 46$ Hz, $J_{PPt} = 2452$ Hz, $Pt-Ph_2P-CH_2-PPh_2$). IR (CH_2Cl_2): $\nu_{CO} = 1998$ (s), 1844 (s), 1806 (s) cm^{-1}. CV (CH_2Cl_2): $E_{1/2} = 0.79$ V, $E_{pa} = 1.83$ V. Anal. Calcd for $C_{53}H_{45}F_6MoO_3P_5Pt{\cdot}CH_2Cl_2$: C, 47.17; H, 3.42. Found: C, 47.80; H, 3.32.

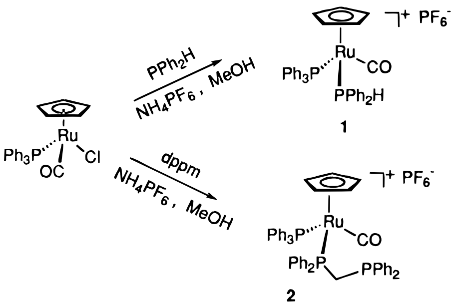
Preparation of [MoCp(CO)₂(*μ*-PPh₂)(*μ*-H)Pt(PPh₃)(MeCN)]PF₆ (8). A Schlenk flask was charged with MoCp(CO)₂(*μ*-PPh₂)(*μ*-H)Pt(PPh₃)Cl (0.50 g, 0.56 mmol, 5:1 mixture of isomers, see eq 8) and MeCN (15 mL). A solution of $TlPF_6$ (0.19 g, 0.56 mmol) in MeCN (5 mL) was added, giving a yellow/orange solution and an off-white precipitate. The mixture was stirred for 30 min, concentrated to *ca.* 10 mL, and filtered through Celite. Evaporating the filtrate to dryness under reduced pressure afforded an orange solid. The solid was recrystallized from CH_2Cl_2/hexane to give 0.55 g of **8** as a mixture of isomers (94% yield). Isomer **A**. ^1H NMR (CD_2Cl_2): δ 7.6−7.1 (m, 25H, PPh_3 and μ-PPh_2), 5.13 (s, 5H, *Cp*), 2.09 (s, 3H, $NCCH_3$), −9.5 (dd, $J_{PP} = 27$, 77 Hz, $J_{PPt} = 477$ Hz, μ-*H*). ^{13}C NMR (CD_2Cl_2): δ 243.6, 193.4 (*C*O), 134−129 (aromatic carbons), 91.9 (Cp), 23.0 (virtual t, $J_{CPt} = 658$ Hz, $NCCH_3$). ^{31}P NMR (CD_2Cl_2): δ 97.6 (s, $J_{PPt} = 3051$ Hz, μ-PPh_2), −35.5 (d, $J_{PP} = 70$ Hz, $J_{PPt} = 4099$ Hz, $Pt-PPh_3$). Isomer **B**. ^1H NMR (CD_2Cl_2): δ 4.76 (s, *Cp*), 1.89 (s, $NCCH_3$), −16.6 (dd, $J_{PP} = 9$, 18 Hz, $J_{PPt} = 680$ Hz, μ-*H*). ^{13}C and ^{31}P NMR peaks for this isomer were not sufficiently resolved for a confident assignment. Mixture **8A**,**B**. CV (CH_2Cl_2): $E_{pa1} = 0.94$ V, $E_{pa2} = 1.13$ V, $E_{pa3} = 1.65$ V, $E_{pa4} = 1.82$ V. IR (CH_2Cl_2): $\nu_{CO} = 1971$ (s), 1905 (s) cm^{-1}. Anal. Calcd for $C_{39}H_{34}NF_6MoO_2P_3Pt$: C, 44.82; H, 3.26; N, 1.34. Found: C, 44.71; H, 3.34; N, 1.14.

Crystal Structure Determination of RuCp(*η*¹-dppm)₂Cl (3). Data were collected at room temperature on a Siemens P3m/V diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\,73$ Å). Thirty-two reflections with $20.0° \leq 2\theta \leq 22.0°$ were used to refine the cell parameters, and 8848 reflections were collected using the ω-scan method. Four reflections were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was <1%). Absorption corrections were applied on the basis of measured crystal faces using *SHELXTL plus*:[19] absorption coefficient, $\mu = 0.56$ mm^{-1} (minimum and maximum transmission factors are 0.883 and 0.946, respectively).

The structure was solved by the heavy-atom method in *SHELXTL plus* from which the location of the Ru atom was obtained. The rest of the non-hydrogen atoms were obtained from a subsequent difference Fourier map. The structure was refined in *SHELXTL plus* using the full-matrix least-squares method. The non-H atoms were treated anisotropically, whereas the positions of the hydrogen atoms were calculated in ideal positions and their isotropic thermal parameters were fixed. A total of 550 parameters were refined, and $\sum w(|F_o| - |F_c|)^2$ was minimized: $w = 1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0.5kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$, I (intensity) = ($I_{peak} - I_{background}$)(scan rate), $\sigma(I) = (I_{peak} + I_{background})^{1/2}$(scan rate), k is the correction due to decay and Lp effects, and 0.02 is a factor used to down-weight intense reflections and to account for instrument instability. The linear absorption coefficient was calculated from values from the *International Tables for X-ray Crystallography*.[20] Scattering factors for non-hydrogen atoms were taken from Cromer and Mann[21] with anomalous-dispersion corrections from Cromer and Liberman,[22] while those of hydrogen atoms were from Stewart, Davidson, and Simpson.[23]

Results and Discussion

Synthesis of Mononuclear Complexes 1−3. Reaction of RuCp(PPh₃)(CO)Cl with NH_4PF_6 in MeOH in the presence of a phosphine results in substitution of phosphine for chloride to yield $RuCp(PPh_3)(CO)L^+$ [L = PPh_2H (**1**) or dppm (**2**)] (eq 3),



(3)

similar to reactions of this starting material reported by Davies and Simpson.[12] The resulting cations, **1** and **2**, are produced in good yield when L = PPh_2H (61%), but much lower yield with L = dppm (14%). Alternatively, **1** could be prepared by reacting RuCp(PPh₃)(CO)Cl and PPh_2H with $TlPF_6$ in CH_2Cl_2, although the yield is slightly lower (58%). Attempts to prepare **2** under the $TlPF_6$/CH_2Cl_2 conditions proved unsuccessful. Analysis of these reaction mixtures, after stirring overnight at room temperature or refluxing 4 h, indicated only unreacted starting material.

The ^1H NMR spectra of both **1** and **2** show numerous aromatic resonances overlapping between 7.8 and 6.9 ppm. Each spectrum also displays a characteristic singlet for the Cp resonance at 5.11 (**1**) or 4.96 ppm (**2**). The phosphine proton of **1** is seen as a doublet of doublets with PH coupling constants of 384 Hz for the attached phosphorus and 8 Hz for the ligated PPh_3. The methylene protons of **2** are seen at 2.70 and 1.79 ppm, also as doublets of doublets, with PH coupling constants of 16 and 10 Hz. In the IR spectrum of **2**, the CO stretch is observed at 1976 cm^{-1}, while that of **1** is at 1989 cm^{-1}, consistent with their formulation as Ru(II) complexes (e.g., for

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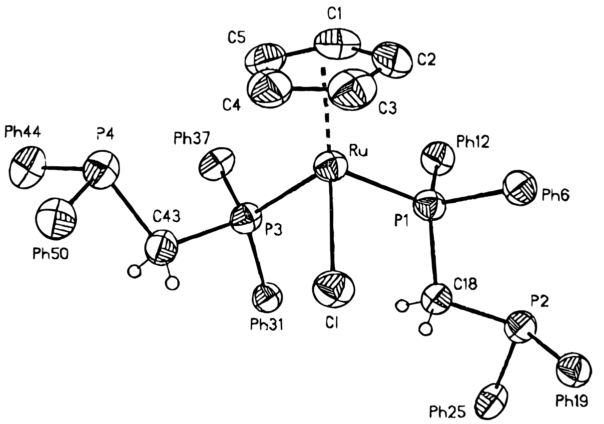


Figure 1. Molecular structure of **3**, with 50% probability ellipsoids, showing the atom numbering scheme. The phenyl groups are symbolized by "Ph" with a number that refers to the C atom bonded to P.

$RuCp(PPh_3)(CO)Cl$ $\nu_{CO} = 1959$ cm^{-1}).[12] The lower energy stretch of the η^1-dppm complex reflects the slightly greater donating ability (or lesser π-acidity) of the dppm ligand relative to that of PPh_2H. This electronic difference is also observed in the oxidation potentials of the compounds (*vide infra*).

Isolation of $RuCp(\eta^1\text{-dppm})_2Cl$ (**3**) from the literature preparation of $[RuCp(\eta^2\text{-dppm})(\eta^1\text{-dppm})]Cl$[13] arose from an attempt to determine the fate of the remaining starting material after the reaction. After precipitation of $[RuCp(\eta^2\text{-dppm})(\eta^1\text{-dppm})]Cl$ in low yield (*ca.* 20%), **3** was obtained from the filtrate in moderate yield (33%) by crystallization. Attempts to improve the yield of **3** by reaction of either $RuCp(PPh_3)_2Cl$ or $RuCp(PPh_3)(\eta^1\text{-dppm})Cl$ with dppm under a variety of conditions gave mixtures of the products noted above in varying ratios; however, the yield of **3** was not improved beyond 33%.

In addition to the aromatic signals for the dppm phenyl groups, the ^1H NMR spectrum of **3** exhibits methylene resonances for the dppm ligand at 3.70 and 1.91 ppm. Both are doublets broadened by ^{31}P coupling. The ^{31}P NMR spectrum shows two widely separated resonances reflecting the differing environments of the phosphorus atoms. The peak at 39.3 ppm is assigned to the Ru-bound phosphorus atoms, while the resonance at −25.2 ppm is assigned to the pendant phosphorus. These assignments correspond with those reported for the closely related compound, $RuCp(PPh_3)(\eta^1\text{-dppm})Cl$.[13]

Structure of $RuCp(\eta^1\text{-dppm})_2Cl$ (3). Shown in Figure 1 is the thermal ellipsoid drawing of complex **3**. The phenyl groups of the dppm ligands have been omitted for clarity, although the phenyl *ipso* carbons (denoted with Ph#) are shown to indicate their position. The unusual η^1 binding mode of both dppm ligands can be seen in Figure 1. There are many examples of bidentate binding of dppm to Ru, but there are only four reported complexes of ruthenium where dppm is in a monodentate binding mode.[24] Although monodentate binding of two dppm ligands has been observed previously in complexes of other metals (i.e., Mo[25] or Re[26]), complex **3** is the first structure reported to have two monodentate dppm ligands coordinated to Ru. The coordination geometry around the metal center is similar to that of $[RuCp(\eta^2\text{-dppm})(\eta^1\text{-dppm})]^{+}$[24a] and is the piano-stool configuration common to four-coordinate Ru−Cp complexes.[27] The Ru atoms in the three other ruthenium structures with a monodentate dppm[24b−d] all display octahedral geometry. Tables 1−3 detail crystallographic data, bond lengths, and bond angles for **3**, respectively.

Table 1. Crystallographic Data for **3**

formula	$C_{55}H_{49}P_4ClRu$	fw, g mol^{-1}	970.34
a, Å	11.490(1)	space group	$P\bar{1}$ (No. 2)
b, Å	14.869(2)	T, °C	25
c, Å	15.447(2)	λ, Å	0.71073
α, deg	84.63(1)	ρ_{calc}, g cm^{-3}	1.355
β, deg	70.55(1)		
γ, deg	72.92(1)	μ cm^{-1}	0.56
V, Å^3	2378.7(5)	R	0.0368^a
Z	2	R_w	0.0415^a

^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

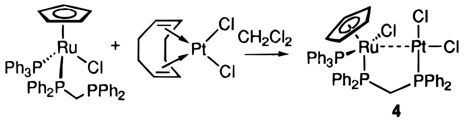
Table 2. Selected Bond Lengths (Å) of Compound **3**

Cl−Ru	2.452(1)	C2−Ru	2.229(5)
P1−Ru	2.319(1)	C3−Ru	2.226(5)
P3−Ru	2.314(1)	C4−Ru	2.221(4)
C1−Ru	2.191(4)	C5−Ru	2.194(3)

Table 3. Selected Bond Angles (deg) of Compound **3**

Cl−Ru−P1	89.91(3)	P1−Ru−P3	97.20(4)
Cl−Ru−P3	87.97(3)		

Synthesis of Heterobimetallic Complexes 4−8. $RuCp(PPh_3)Cl(\eta^1\text{-dppm})$ reacts readily with $Pt(COD)Cl_2$ to give the heterobinuclear complex $RuCp(PPh_3)Cl(\mu\text{-dppm})PtCl_2$ (**4**) (eq 4) in which the diene has been displaced from platinum. This yellow compound is air stable as a solid, although solutions decompose slowly over the course of a day when exposed to air. The ^{31}P NMR spectrum of complex **4** has resonances at 49.1 and 37.8 ppm assigned to the Ru-bound dppm phosphorus and the PPh_3, respectively. A peak at −2.9 ppm shows satellites ($J_{PPt} = 3826$ Hz) characteristic of platinum coupling and is therefore assigned to the dppm phosphorus bound to Pt. The ^1H and ^{13}C NMR spectra are less diagnostic, yet do display signals at 2.71 and 82 ppm, respectively, due to the dppm methylene bridge.[28]



(4)

In a reaction similar to the preparation of **4**, the bis η^1-dppm ruthenium compound, **3**, reacts with $Pt(PhCN)_2Cl_2$ in CH_2Cl_2 to give the neutral bimetallic complex, $RuCpCl(\mu\text{-dppm})_2PtCl_2$ (**5**) (eq 5). However, when **3** is combined with $Pt(COD)Cl_2$, no bimetallic complex is formed. Rather, transfer of dppm from $RuCpCl(\eta^1\text{-dppm})_2$ (**3**) to platinum occurs, leading to $RuCpCl(\eta^2\text{-dppm})$ and $Pt(\eta^2\text{-dppm})Cl_2$. Confirmation of the identity of these products was made by comparison of the spectral data with that reported in the literature.[13,29]

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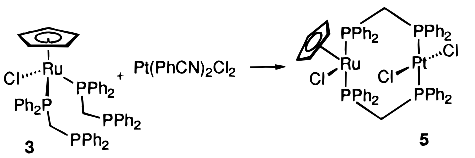
(28) A reviewer has suggested an alternative structure for **4** in which the ruthenium−chloride is bridging. This structure cannot be excluded on the basis of the spectroscopic data. However, subsequent manipulation of the complex suggests the Ru-bound chloride is the most reactive of the three chlorides (*vide infra*). In the absence of crystallographic data, we conclude that the structure pictured in eq 4 is more likely.

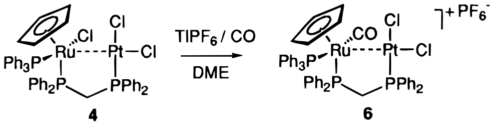


3 5 (5)

The aromatic region of the ^{1}H NMR spectrum of **5** is predictably crowded. However, the Cp resonance is well resolved at 5.03 ppm, as is the multiplet for the methylene protons of the dppm bridges at 3.21 ppm. The ^{13}C NMR spectrum exhibits a similar pattern in that the aromatic carbon resonances are overlapping while the Cp and methylene resonances are more distinct at 91.3 and 61.8 ppm, respectively. The platinum satellites bracketing the doublet at −2.6 ppm ($J_{\mathrm{PPt}} = 2372$ Hz) in the ^{31}P spectrum identify the resonance as that for the Pt-bound phosphorus. The resonance at 43.2 ppm is similar to those of other Ru-bound phosphines.

As one goal of this work is to ligate putative intermediates from the oxidation of methanol, methoxide (or other alkoxides) and CO were chosen as target ligands. Attempts to substitute an alkoxide for a chloride on complex **4** with TlOEt, TlOMe, $\mathrm{TlO^tBu}$, or $\mathrm{NH_4PF_6}$ in $\mathrm{CH_2Cl_2}$, MeOH, or combinations of these solvents produced no identifiable substitution products. In addition, mixtures of **4** in MeOH with either a catalytic or equimolar amount of a hindered amine (proton sponge, $\mathrm{NEt_3}$) failed to produce any substitution product. The extremely low solubility of **4** in MeOH, however, may preclude reactions in this solvent.

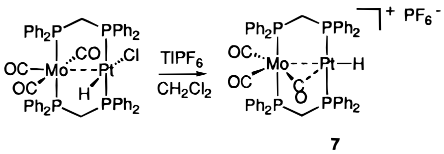
Reaction of **4** with $\mathrm{TlPF_6}$ in the presence of CO results in substitution of a single chloride on **4** at the ruthenium center to form $[\mathrm{RuCp(CO)(PPh_3)}(\mu\text{-dppm})\mathrm{PtCl_2}]\mathrm{PF_6}$ (**6**) (eq 6). Assignment of the site of CO binding is based on spectroscopic and electrochemical data for the complex. The carbonyl peak in the ^{13}C NMR spectrum shows no platinum satellites; however, we cannot rule out the possibility that such satellites may be lost in the baseline due to the low signal to noise ratio of the peak. The IR spectrum of **6** shows a CO band ($\nu_{\mathrm{CO}} = 1979$ cm^{-1}) remarkably similar to that of the similarly ligated compound $[\mathrm{RuCp(PPh_3)CO}(\eta^1\text{-dppm})]\mathrm{PF_6}$ (**2**) ($\nu_{\mathrm{CO}} = 1976$ cm^{-1}). In addition, there is a significant shift in the oxidation potential of the ruthenium center (see Electrochemistry section). These data suggest the structure as drawn in eq 6 rather than one with the carbonyl bound to platinum.



4 6 (6)

With 1 equiv of $\mathrm{TlPF_6}$, **6** is the only CO-substituted product isolated. When 2 equiv of $\mathrm{TlPF_6}$ are used in the reaction, a mixture of products containing **6** and a number of other compounds results. Three equivalents of $\mathrm{TlPF_6}$ give only unidentified decomposition products. If the reaction is carried out in $\mathrm{CH_2Cl_2}$ instead of DME, $\mathrm{TlPF_6}$ reacts with **4** to give a product in which chloride has been abstracted, as evidenced by the TlCl filtered from the reaction. The product could not be fully characterized, but an IR spectrum of the product indicates no incorporation of CO.

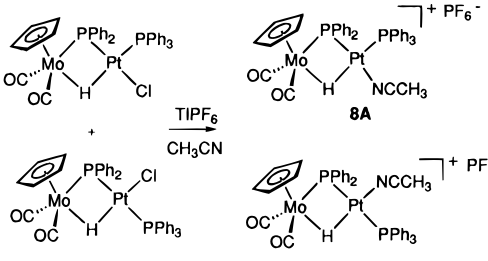
The known heterobinuclear complex, $\mathrm{Mo(CO)_3}(\mu\text{-dppm})_2\mathrm{Pt(H)Cl}$, reacts with $\mathrm{TlPF_6}$ in $\mathrm{CH_3CN}$ or $\mathrm{CH_2Cl_2}$ to yield TlCl and the cation $[\mathrm{Mo(CO)_3}(\mu\text{-dppm})_2\mathrm{Pt(H)}]\mathrm{PF_6}$ (**7**) (eq 7) in high yield (90%). No incorporation of $\mathrm{CH_3CN}$ was indicated by ^{1}H NMR analysis of the complex when this solvent was used.



7 (7)

On the basis of spectroscopic data, assignment of structure **7** is as shown in eq 7. The ^{31}P NMR spectrum shows the multiplet characteristic of $\mathrm{PF_6^-}$ at 350.2 ppm which confirms the cationic nature of the compound. The IR spectrum shows two CO bands typical for terminal carbonyl ligands[30] (1998 and 1844 cm^{-1}) and one band of lower energy at 1806 cm^{-1}. In addition, the ^{13}C NMR spectrum shows a peak at 190.8 ppm, which is at lower field than the typical carbonyl carbon resonance. The presence of an open coordination site on Pt, as well as these data, suggests that one carbonyl may be bridging or semibridging. However, spectral data for terminal carbonyls overlap[31] with those observed here, making a conclusive assignment of the bonding of one CO impossible in the absence of structural data.

In a related reaction, $\mathrm{MoCp(CO)_2}(\mu\text{-PPh_2})(\mu\text{-H})\mathrm{Pt(PPh_3)Cl}$ (mixture of isomers) was combined with $\mathrm{TlPF_6}$ in $\mathrm{CH_3CN}$. In this case, chloride abstraction occurred with incorporation of acetonitrile to give $[\mathrm{MoCp(CO)_2}(\mu\text{-PPh_2})(\mu\text{-H})\mathrm{Pt(PPh_3)(CH_3CN)}]\mathrm{PF_6}$ (**8**) (eq 8). The product is a mixture of isomers (**A**, $\mathrm{PPh_3}$ and μ-$\mathrm{PPh_2}$ are *cis*; **B**, MeCN and μ-$\mathrm{PPh_2}$ are *cis*) in a *ca.* 5:1 ratio (**A**:**B**) and reflects the ratio observed in the starting material.



8A 8B (8)

The ^{31}P NMR spectrum of the mixture of **8A** and **8B** shows the bridging phosphido resonance of **8A** at 97.6 ppm, markedly shifted from the analogous resonance in the starting material (167 ppm). The bridging hydride resonances observed in the ^{1}H NMR spectrum of the mixture were assigned by comparison of the chemical shifts and $^{195}\mathrm{Pt}-^1\mathrm{H}$ coupling constants (**A**, −9.5 ppm, $J_{\mathrm{PtH}} = 477$ Hz; **B**, −16.6 ppm, $J_{\mathrm{PtH}} = 680$ Hz) with those of the analogous isomers of the starting material (**A**, −8.40 ppm, $J_{\mathrm{PtH}} = 445$ Hz; **B**, −15.6 ppm, $J_{\mathrm{PtH}} = 684$ Hz).[10a]

Electrochemistry. Cyclic voltammetric results for the ruthenium monomers **1**−**3** are summarized in Table 4. The compounds with a coordinated CO (**1** and **2**) exhibit irreversible oxidation potentials at 1.95 and 1.91 V, respectively. The potentials reflect the electronic trend of the $\mathrm{PPh_2H}$ ligand and η^1-coordinated dppm ligand observed in the ν_{co} values.

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Table 4. Summary of Redox Potentials for Monomeric Compounds[a]

compound	redox change	$E_{1/2}$ (V vs NHE)	ref
$[RuCp(Ph_3P)(CO)(PPh_2H)]PF_6$ (**1**)	Ru(II/III)	1.95[b]	*c*
$[RuCp(Ph_3P)(CO)(\eta^1\text{-dppm})]PF_6$ (**2**)	Ru(II/III)	1.91[b]	*c*
$RuCpCl(\eta^1\text{-dppm})_2$ (**3**)	Ru(II/III)	0.50	*c*
$RuCpCl(PPh_3)(\eta^1\text{-dppm})$	Ru(II/III)	0.56	13
$MoCp(NO)I_2(PMePh_2)$	Mo(IV/III)	−1.22	32
$MoCp(NO)Cl_2$	Mo(IV/III)	−0.34	32
$Mo(CO)_2Cl_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})$	Mo(II/III)	1.20[b]	33
$Mo(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})$	Mo(II/I)	0.42	34
cis-$PtCl_2(PMePh_2)_2$	Pt(II/IV)	2.19[b,d]	35
trans-$PtCl_2(PMePh_2)_2$	Pt(II/IV)	1.59[b,d]	35
cis-$PtCl_2(PPh_3)_2$	Pt(II/IV)	2.24[b,d]	35
trans-$PtCl_2(PPh_3)_2$	Pt(II/IV)	1.79[b,d]	35
trans-$Pt(PPh_3)_2$ (H)Cl	Pt(II/IV)	1.68[b]	36
$Pt(\eta^2\text{-dppm})Cl_2$	Pt(II/IV)	2.01[b]	29

[a] All values obtained in CH_2Cl_2/TBAH unless otherwise noted. [b] Irreversible wave, E_{pa} reported. [c] This work. [d] CH_3CN/TBAP, Pt working electrode.

Table 5. Summary of Redox Potentials for Bimetallic Compounds (CH_2Cl_2/TBAH)

compound	redox change	$E_{1/2}$ (V vs NHE)	ref
$RuCp(PPh_3)Cl(\mu\text{-dppm})PtCl_2$ (**4**)	Ru(II/III)	1.13	*b*
	Pt(II/IV)	1.78[a]	
$RuCpCl(\mu\text{-dppm})_2PtCl_2$ (**5**)	Ru(II/III)	1.13[a]	*b*
	Pt(II/IV)	1.45[a]	
$[RuCp(PPh_3)CO(\mu\text{-dppm})PtCl_2]PF_6$ (**6**)	Ru(II/III)	1.43[a]	*b*
	Pt(II/IV)	1.68[a]	
$[Mo(CO)_3(\mu\text{-dppm})_2Pt(H)]PF_6$ (**7**)	Mo(0/I)	0.79	*b*
	Pt(II/IV)	1.83[a]	
$Mo(CO)_3(\mu\text{-dppm})_2Pt(H)Cl$	Mo(0/I)	0.38	16
	Pt(II/IV)	1.44[a]	
$[MoCp(CO)_2(\mu\text{-PPh}_2)(\mu\text{-H})Pt(PPh_3)(CH_3CN)]PF_6$ (**8**)	Mo(II/III)	0.94[a]	*b*
	Mo(II/III)	1.13[a]	
	Pt(II/IV)	1.65[a]	
	Pt(II/IV)	1.82[a]	
$MoCp(CO)_2(\mu\text{-PPh}_2)(\mu\text{-H})Pt(PPh_3)Cl$	Mo(II/III)	0.98[a]	17
	Mo(II/III)	1.15[a]	
	Pt(II/IV)	1.36[a]	
	Pt(II/IV)	1.53[a]	
$[MoCp(CO)_2(\mu\text{-PPh}_2)(\mu\text{-H})Pt(PPh_3)_2]PF_6$	Mo(II/III)	1.16[a]	17
	Pt(II/IV)	2.03[a]	

[a] Irreversible wave, E_{pa} reported. [b] This work.

The oxidation potential of $RuCpCl(\eta^1\text{-dppm})_2$ (**3**) is negative of that of **1** and **2** at 0.50 V**.** Such a shift is expected for a compound with greater electron density at the metal center.

Cyclic voltammetric results for the heterobimetallic compounds (**4**−**8**) are summarized in Table 5. The cyclic voltammetric scan of $RuCp(PPh_3)Cl(\mu\text{-dppm})PtCl_2$ (**4**) (Figure 2) shows a couple at 1.13 V vs NHE and an electrochemically irreversible oxidation wave at 1.78 V in CH_2Cl_2. The 1.13 V couple is fully reversible if the switching potential of the scan is <1.6 V, and is assigned to the ruthenium(II/III) couple, while the irreversible wave is assigned to the Pt(II/IV) oxidation. The II/III wave of the monomeric ruthenium compound, $RuCp(PPh_3)Cl(\eta^1\text{-dppm})$, is observed at 0.56 V.[13] Considering the minor change in the ligand geometry about ruthenium, the nearly 600 mV shift positive in its oxidation potential indicates a significant loss in electron density at the metal. Donation of this density to a Ru−Pt interaction accommodates the coordinatively unsaturated platinum center and suggests the structure of the compound as drawn in eq 4. Further evidence of such an interaction comes from the oxidation wave from the platinum center. The Pt oxidation at 1.78 V contrasts with that of the starting material, $Pt(COD)Cl_2$, which shows no oxidation wave in the solvent window of CH_2Cl_2 (>2.0 V). Interestingly, compounds which should contain a more electron rich platinum coordination environment than **4** due to the presence of two phosphines [e.g., $PtCl_2(PMePh_2)_2$, $Pt(PPh_3)_2(H)Cl$] display oxidation potentials similar to that observed in **4** (see Table 4). This also suggests that electron density is donated from Ru to Pt.

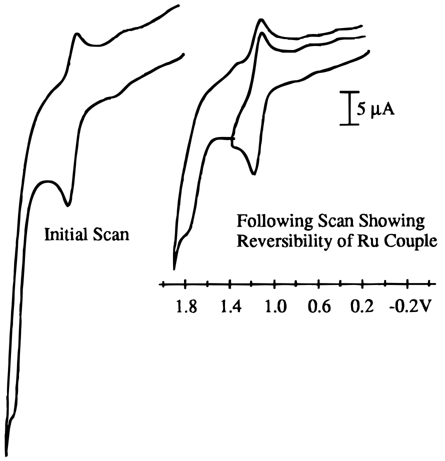

Figure 2. Cyclic voltammograms of **4** in CH_2Cl_2/TBAH (V vs NHE, Glassy carbon electrode, 100 mV/s, ambient *T*).

Replacement of a chloride on the bimetallic Ru/Pt compound **4** with CO leads to **6** and produces a significant shift in the oxidation potentials of the compound. The Ru(II/III) potential of **6** shifts 300 mV positive of that of **4**, while the Pt(II/IV) oxidation shifts 100 mV negative of that of the starting material. Both shifts are consistent with the notion of the CO being ligated to ruthenium and support the structure postulated earlier. The π-back-bonding nature of CO, as well as the cationic Ru center, contributes to the more positive oxidation potential of the metal. The negative shift in the irreversible Pt wave may be rationalized by solvent coordination in the absence of a suitable metal−metal interaction. Conversely, if the carbonyl were bound to platinum, the potentials would both be expected to shift positive of that of the starting material, with the Pt shift being greater than that of Ru.

The cyclic voltammogram of $[Mo(CO)_3(\mu\text{-dppm})_2Pt(H)]PF_6$ (**7**) exhibits a reversible couple at 0.79 V and an electrochemically irreversible wave at 1.83 V. The reversible couple is assigned to the molybdenum center while the irreversible wave is assigned to the platinum center. The oxidation potential of the cationic Pt center is nearly 400 mV positive of that of the neutral bimetallic starting material, $Mo(CO)_3(\mu\text{-dppm})_2Pt(H)Cl$, though similar to the neutral monomer, *trans*-$PtCl_2(PPh_3)_2$, at 1.79 V.[35] The Mo(0/I) potential of **7** is in marked contrast to both the irreversible oxidation potential of the similar monomer, $Mo(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})$ (see Table 4), at 0.42 V and the reversible Mo(0/I) couple of the starting material, $Mo(CO)_3(\mu\text{-dppm})_2Pt(H)Cl$, at 0.38 V. Loss of a chloride from **7** creates both a cationic complex and an open coordination site on Pt. The shift in the Mo(0/I) potential could be explained by a new metal−metal interaction or a bridging or semibridging carbonyl. A bridging carbonyl alone would satisfy the Pt coordination sphere, but would not account for the positive shift in Mo potential, since a bridging CO is poorer at π-back-bonding than a terminal CO. These data, taken along with the spectroscopic evidence, suggest that a structure with a bridging carbonyl, as well as a Mo/Pt interaction, is most consistent with the data.

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Unlike the Mo(0)/Pt(II) complex (**7**), the CV of $[MoCp(CO)_2(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)(CH_3CN)]PF_6$ (**8**) shows two irreversible waves at 0.94 and 1.13 V for the Mo(II/III) oxidations of the *trans* and *cis* isomers, respectively. The Pt(II/IV) oxidations are observed at 1.65 and 1.82 V for the *trans* and *cis* isomers, respectively. These assignments correspond with reported trends for *trans* and *cis* forms of four-coordinate Pt oxidation potentials.[35,37] Substitution of CH_3CN for Cl^- at the platinum center has little effect on the oxidation potentials of the molybdenum center, as can be seen when the Mo(II/III) potentials of $MoCp(CO)_2(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)Cl$ and **8** are compared (Table 5). However, a positive shift in the Pt potentials is observed, generally consistent with the notion of a cationic compound being more difficult to oxidize. Also noteworthy is the difference in the Mo oxidation potentials of **8A**,**B** and $[MoCp(CO)_2(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]PF_6$. The complexes are each cationic and the molybdenum coordination spheres identical, yet there is a difference of 220 mV in the oxidation potential of one isomer (**8B**) and the platinum bis(phosphine) compound, while the potential of the second isomer (**8A**) is nearly identical to that of the reference compound. These differences in oxidation potential emphasize the propensity of the metal centers to "communicate" through the bridging ligands, since the only change in the compounds occurs at platinum.

Conclusions

In the compounds investigated here, the platinum oxidation potentials appear to be relatively insensitive to the redox potential of the second metal when the possibility for a metal–metal interaction is precluded. For example, compare the Pt oxidation potential of **5** (1.45 V) with that of $Mo(CO)_3(\mu\text{-}dppm)_2Pt(H)Cl$ (1.44 V). Although the metal bridged to platinum in the two complexes is different, as is the oxidation state of each, the redox potentials of the similarly ligated Pt centers are nearly identical. When an opportunity for a metal–metal interaction exists, the Pt oxidation potential displays a large dependence on the second metal's redox state, illustrating the influence each center has on the other. The shift in the oxidation potentials of **4** and **6** exemplify this influence. One should be able, in such complexes, to exploit this dependence by doing chemistry at one metal center with the intent of tuning the redox potential of the second metal. Such an approach may provide further insight into the redox properties of heterobimetallic systems in which one metal is a reactive site but chemically inaccessible through common methods.

Acknowledgment. Funding for this work was provided by the Division of Sponsored Research, University of Florida. K_2PtCl_4, $PtCl_2$, and $RuCl_3 \cdot xH_2O$ were generously supplied by the Johnson Matthey Metals Loan Program.

Supporting Information Available: Complete thermal ellipsoids drawing, tables of bond lengths and angles, and crystallographic data for **3** (15 pages). Ordering information is given on any current masthead page.

IC9510977

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