are presaturated, only the resonances at 6.76 ppm showed NOE, allowing assignment of this set of resonances to H_6. Presaturation of the methylene protons of the ethyl group showed only H_4 to give appreciable NOE, locating the ethyl group on C_3. Similar NOE measurements were carried out on other products and their regioisomers determined.

We are studying the mechanism of this reaction and the influence of other tridentate ligands and nucleophiles.

Acknowledgment. We thank Drs. C.-L. Wang, D. C. Roe, D. L. Thorn, and H. E. Bryndza and Professor B. M. Trost for interesting discussions and B. D. Johnson for technical assistance.

Registry No. EtBr, 74-96-4; MeI, 74-88-4; $PhCH_2Cl$, 100-44-7; PhBr, 108-86-1; *n*-BuCl, 109-69-3; [Ni(triphos)Cl]PF_6, 33847-47-1; *sec*-BuCl, 78-86-4; $NiCl_2$(dppp), 15629-92-2; *o*-dichlorobenzene, 95-50-1; *m*-dichlorobenzene, 541-73-1; *p*-dichlorobenzene, 106-46-7; 2,6-dichloroanisole, 1984-65-2; 2,6-dichlorotoluene, 118-69-4; 3,4-dichlorotoluene, 95-75-0; 2,4-dichlorobenzotrifluoride, 320-50-3; 2,5-dichlorotoluene, 19398-61-9; 2,4-dichlorotoluene, 95-73-8; 2,3-dichloroanisole, 1984-59-4; *o*-chloroethylbenzene, 89-96-3; *o*-diethylbenzene, 135-01-3; *o*-chlorotoluene, 95-49-8; *o*-xylene, 95-47-6; *o*-chloro-*sec*-butylbenzene, 36383-12-7; *o*-di-*sec*-butylbenzene, 1013-03-2; *o*-chlorobenzylbenzene, 29921-41-3; *o*-dibenzylbenzene, 792-68-7; *o*-chlorobiphenyl, 2051-60-7; *o*-diphenylbenzene, 84-15-1; *m*-chlorobutylbenzene, 15499-28-2; *m*-dibutylbenzene, 17171-74-3; *m*-chloro-*sec*-butylbenzene, 36383-13-8; *m*-di-*sec*-butylbenzene, 1079-96-5; *p*-chloroethylbenzene, 622-98-0; *p*-diethylbenzene, 105-05-5; *p*-chloro-*sec*-butylbenzene, 36383-14-9; *p*-di-*sec*-butylbenzene, 1014-41-1; 6-chloro-2-ethylanisole, 89031-98-1; 2,6-diethylanisole, 2944-51-6; 2-butyl-6-chlorotoluene, 89031-99-2; 2,6-dibutyltoluene, 89032-00-8; 1-butyl-2-*sec*-butylbenzene, 89032-01-9; bibenzyl, 103-29-7; 1-*sec*-butyl-3-butylbenzene, 89032-02-0; 1-*sec*-butyl-4-butylbenzene, 37909-91-4; 3-ethyl-4-chlorotoluene, 89032-03-1; 3,4-diethyltoluene, 13732-80-4; 2-chloro-5-ethylbenzotrifluoride, 89032-04-2; 2-ethyl-5-chlorobenzotrifluoride, 89032-05-3; 2,5-diethylbenzotrifluoride, 89032-06-4; 2-ethyl-5-chlorotoluene, 89032-07-5; 2-chloro-5-ethyltoluene, 89032-08-6; 2,5-diethyltoluene, 13632-94-5; 2-ethyl-4-chlorotoluene, 89032-09-7; 2-chloro-4-ethyltoluene, 89032-10-0; 2,4-diethyltoluene, 1758-85-6; 2-chloro-3-ethylanisole, 89032-11-1; 2-ethyl-3-chloroanisole, 89032-12-2.

Organometallic Chemistry in Aqueous Solution: Water-Soluble Bis(dimethylphosphino)methane-Bridged Dipalladium Complexes†

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Summary: A new series of binuclear palladium complexes bridged by the diphosphine bis(dimethylphosphino)methane (dmpm) is reported. The complex, $Pd_2Cl_2(dmpm)_2$, has been prepared and found to have remarkably high solubility and stability in aqueous solutions. In aqueous solutions, the complex exists as $Pd_2(OH)_2(dmpm)_2$ at pH > 4. In either aqueous or nonaqueous solvents, $Pd_2X_2(dmpm)_2$ (X = Cl, OH, OR) inserts one equivalent of CO into its Pd–Pd bond to give $Pd_2X_2(\mu\text{-}CO)(dmpm)_2$. The structure of $Pd_2Cl_2(\mu\text{-}CO)(dmpm)_2$ has been determined by X-ray diffraction.

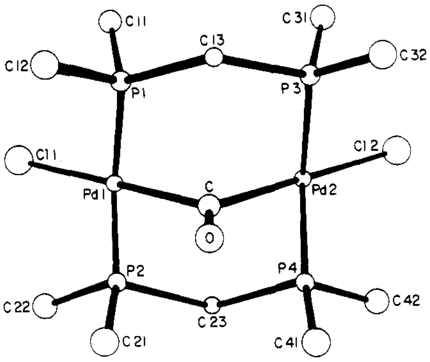

Figure 1. Drawing of $Pd_2Cl_2(\mu\text{-}CO)(dmpm)$ with all non-hydrogen atoms.

We report the synthesis and reactivity of bis(dimethylphosphino)methane-bridged binuclear palladium complexes which have an unusual property: high solubility in aqueous solutions. Numerous reports of diphosphine-bridged binuclear transition-metal complexes have appeared in recent years.[1-26,32] The impetus for many of

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† This paper is dedicated to the memory of Professor Earl L. Muetterties.

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(27) $Pd_2Cl_2(dmpm)_2$: Anal. Calcd for $C_{10}H_{28}P_4Cl_2Pd_2$: C, 21.60; H, 5.08. Found: C, 21.92; H, 5.25. ^1H NMR (CD_2Cl_2) δ 2.65 (m), 1.60 (m); ^1H NMR (D_2O) δ 2.80 (m), 1.57 (m); $^{13}C\{^1H\}$ NMR (CH_2Cl_2) δ 42.0 (CH_2, t), 16.9 (CH_3, q); $^{31}P\{^1H\}$ NMR (H_3PO_4 external, CD_2Cl_2/CH_2Cl) δ −31 (s); $^{31}P\{^1H\}$ NMR (D_2O) δ −33 (s); IR (CD_3CN) 1420 (w), 1300 (w), 1290 (w), 1290 (w), 1180 (m) cm^{-1}; UV–vis (λ_{max}, nm (ϵ)) (H_2O) 261 (17 000), 290 (9890), 339 (4670), 393 (2760), (CH_3CN) 242 (8899), 274 (17 909), 318 (9948), 382 (4531), (CH_2Cl_2) 243 (10 863), 278 (22 383), 320 (14 167), 385 (5729); $\Lambda_{0.001M} = 51.5\ \Omega^{-1}\ cm^2\ mol^{-1}$ in H_2O.

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these studies has been the need to identify the chemistry of discrete, interacting dimetallic sites, which relate to catalytic reactions occurring on metal surfaces. Our present study is among the first dealing with complexes bridged by the relatively sterically undemanding alkyl diphosphine bis(dimethylphosphino)methane (dmpm). Recently Karsch[33] and Puddephatt[36,37] reported the preparation and structure of dmpm-bridged Ag and Pt complexes, respectively.

The new palladium complex, Pd_2Cl_2 $(dmpm)_2$ (**1**), was prepared by addition of a slurry of $[Pd(CO)Cl]_n$[30] to a CH_2Cl_2 solution of dmpm at −75 °C. The solution was concentrated and diethyl ether added to precipitate a yellow-orange solid. The solid was dried in vacuo, giving yields of 60–90%. **1** has the composition $C_{10}H_{28}P_4Cl_2Pd_2$ and has been characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR, IR, and UV–vis spectroscopy[27] as well as by Raman spectroscopy.[40]

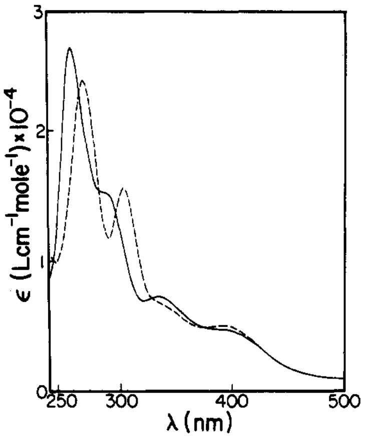

Figure 2. UV–vis spectra of $Pd_2Cl_2(dmpm)_2$ in H_2O (—) and in aqueous 1 M NaCl (- - -). In the absence of Cl^-, the principal species in aqueous solution is $Pd_2(OH)_2(dmpm)_2$. The addition of Cl^- shifts the equilibrium such that the principal species in solution is $Pd_2Cl_2(dmpm)_2$.

Complex **1** readily adds 1 equiv of CO to give Pd_2Cl_2-$(\mu\text{-}CO)(dmpm)_2$[28] (**2**), which exhibits $\nu(CO) = 1710$ cm^{-1} and has been characterized by X-ray diffraction.[31] The structure of **2** is presented in Figure 1. The molecule possesses an "A frame" structure[6] with two Pd centers having approximately square-planar geometries and sharing a common carbonyl ligand. The Pd···Pd separation is 3.169 (1) Å, which suggests a nonbonding metal–metal interaction. The structure of **2** has no crystallographically imposed symmetry. The bridging CO is slightly asymmetric, with bond distances Pd1–C(1) 1.988 (10) and Pd2–C(1) 1.948 (11) Å and bond angles Pd1–C(1)–O(1) 122.77 (88), Pd2–C(1)–O(1) 130.00 (84), and Pd1–C(1)–Pd2 107.23 (52)°. The C(1)–O(1) bond distance is 1.180 (12) Å.

Complex **1** is reactive with respect to the addition of numerous other small molecules. For example, $\mu\text{-}SO_2$[38] and $\mu\text{-}CS_2$[39] complexes have been obtained as analytically pure, crystalline solids and characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR. Complex **1** also forms stable 1:1 complexes with H_2C_2[45] CNMe.[46] The addition of small molecules to the Pd–Pd bond of **1** parallels the addition of SO_2,[13] CNMe,[5] and acetylenes[34] to the Pd–Pd bonds and of CS_2[29] to the Pt–Pt bonds of related dppm- (bis(diphenylphosphino)methane) bridged complexes.

A most surprising departure in the chemistry of **1** compared to its dppm-bridged relatives is its reactivity with water. Complex **1** is unusually soluble and stable in aqueous solutions. The ^1H and $^{31}P\{^1H\}$ NMR data for **1**

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(28) Pd_2Cl_2 $(\mu\text{-}CO)(dmpm)_2$: Anal. Calcd for $C_{11}H_{28}OP_4Cl_2Pd_2$: C, 22.61; H, 4.83. Found: C, 22.35; H, 4.58. ^1H NMR (CD_2Cl_2) δ 2.71 (m), 1.61 (m), 1.48 (m); $^{31}P\{^1H\}$ NMR (H_3PO_4 external, CD_2Cl_2/CH_2Cl_2) δ 1.28 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 244 (q, $J = 5.3$ Hz), 41.9 (CH_2, m), 16.9 (CH_3, q, $J = 8.7$ Hz), 13.8 (CH_3, m); IR (CD_2Cl_2) 1710 (s), 1415 (m), 1290 (m) 1260 (m), 1180 (w), 1140 cm^{-1} (w); UV–vis(λ_{max}, nm (ε)) (CH_2Cl_2) 241 (18 400), 284 (11 000), 383 (6000), 444 (11 700), (CH_3CN) 239 (15 200), 284 (8700), 386 (4800), 442 (8800).

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(31) Complex **2** crystallized in the space group $P_{2_12_12_1}$ with $a = 15.511$ (2), $b = 11.107$ (2), $c = 12.346$ (2) Å, $Z = 4$, $\rho_{calcd} = 1.80$ g/cm^3, $\rho_{obsd} = 1.83$ g/cm^3 for the formula unit $Pd_2Cl_2P_4(CO)C_{10}H_{28}$. Intensity data were collected by using Mo Kα radiation by the ω-scan technique in the range $3° < 2\theta < 54°$ on a locally modified Enraf-Nonius CAD-4 diffractometer. A total of 2534 unique reflections from the octant ($+h$, $+k$, $+l$) have been obtained. Three standard reflections were monitored every 100 reflections and showed no evidence of crystal decomposition. The structure was solved by MULTAN–least-squares–Fourier methods and is refined presently to R_1 and R_2 values of 0.048 and 0.070, respectively, for 131 parameters and 1784 observations with $F^2 > 3\sigma(F^2)$. The heavy atoms Pd, Cl and P along with the bridging C and O atoms were refined anisotropically while all other carbon atoms were refined isotropically. The H atoms were not located. The linear absorption coefficient $\mu = 22$ cm^{-1}, and therefore no absorption correction was made. The extimated maximum and minimum T are 0.64 and 0.52 respectively. The quantities minimized were $R^1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$ where $w = 1/[\sigma(I)^2 + (0.04\ F^2)^2]^{1/2}$. The esd of an observation of unit weight is presently 2.43. The programs used to solve the structure were part of the Structure Determination Package of B. A. Frenz and Associates, College Station, TX, and Enraf-Nonius, Delft, Holland. All calculations were performed on a DEC 11/60 computer in the Purdue University Department of Chemistry X-ray Diffraction Facility. Tables, including thermal parameters of all atoms, their atomic positions, all bond lengths and angles, and observed and calculated structure factors, are found in the supplementary section of this paper.

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(38) $Pd_2(\mu\text{-}SO_2)Cl_2(dmpm)_2$: Anal. Calcd for $C_{10}H_{28}P_4Cl_2SO_2Pd_2$: C, 19.37; H, 4.55. Found: C, 19.83; H, 4.33. ^1H NMR (CD_2Cl_2) δ 2.34 (m), 1.62 (m), 1.39 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, H_3PO_4 external) δ 9.04 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 25.74 (CH_2, m), 15.23 (CH_3, m), 13.13 (CH_3, m); IR (Nujol) 1150 (m), 1030 (m) 940 (m) cm^{-1}.

(39) $[Pd_2Cl_2(\mu\text{-}CS_2)(dmpm)_2]\cdot{}^1/_2(CH_3CH_2)_2O$: Anal. Calcd for $C_{13}H_{33}P_4S_2Cl_2O_{0.5}Pd_2$: C, 23.30; H, 4.97. Found: C, 23.23; H, 5.17. ^1H NMR (CD_2Cl_2) δ 2.39 (m), 1.79 (m), 1.63 (m), 1.45 (m); $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2) δ 27.96 (CH_2, m), 12.86 (CH_3, m); $^{31}P\{^1H\}$ NMR (H_3PO_4 external, CD_2Cl_2/CH_2Cl_2) δ −8.83 (m); IR (Nujol) 935, 1010 cm^{-1}.

(40) The Raman spectrum of $Pd_2Cl_2(dmpm)_2$ in CH_2Cl_2 exhibits ν(Pd–Pd) = 140 and ν(Pd–Cl) = 257 cm^{-1}. Raman spectra of related Pd–Pd bonded complexes: $Pd_2Cl_2(dppm)_2$ in CH_2Cl_2 ν(Pd–Pd) = 140 and ν(Pd–Cl) = 236 cm^{-1}; $Pd_2Cl_2(dmpm)_2$ in H_2O ν(Pd–Pd) = 140 and ν(Pd–O) = 351 cm^{-1}; $Pd_2Br_2(dppm)_2$ (CH_2Cl_2) ν(Pd–Pd) = 138 and ν(Pd–Br) = 161 cm^{-1}; $Pd_2Br_2(dmpm)$ (CH_2Cl_2) ν(Pd–Pd) = 123 and ν(Pd–Br) = 169 cm^{-1}.

(41) $Pd_2(OH)_2(\mu\text{-}CO)(dmpm)_2$ ^1H NMR (D_2O) δ 3.04 (m), 2.10 (s), 1.57 (m); $^{31}P\{^1H\}$ NMR (D_2O, H_3PO_4 external) 3.56 (s); $^{13}C\{^1H\}$ NMR (D_2O) δ 246 (q, $J_{PC} = 5.4$ Hz), 168.06 (m), 39.56 (CH_2, m), 15.50 (CH_3, m), 11.75 (CH_3, m); UV–vis (λ_{max}, nm (ε))(H_2O) 221 (18 000), 292 (12 000), 372 (4000), 498 (1700). The resonance at δ 168.06 in the $^{13}C\{^1H\}$ NMR spectrum may correspond to some small degree of CO insertion into the Pd–O bonds of **5**.

(42) IR (CH_3CN) 1585 (s), 1290 (s, br), 1185 (s), 1170 (s), 1130 (w); ^1H NMR (CD_2Cl_2) δ 7.15 (m), 6.80 (m), 1.64 (m).

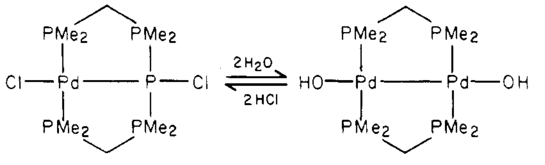
(43) IR (CH_3CN) 1780 (s), 1715 (m), 1605 (s), 1595 (s) 1290 (w), 1265 (s), 1225 (s), 1170 (w) cm^{-1}; ^1H NMR (CH_3CN) δ 7.20 (m), 6.85 (m); $^{31}P\{^1H\}$ NMR (CD_3CN,H_3PO_4 external, ^{13}CO enriched) δ 4.2 (ddd); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 244 (q, $J_{PC} = 5.2$ Hz), 158 (s), 130 (s), 126 (s), 120 (s), 116 (s).

(44) IR (CH_3CN) 1715 (m), 1605 (sh), 1595 (s), 1295 (s), 1265 (s), 1220 (s), 1170 (s, br) cm^{-1} ^1H NMR (CH_3CN) δ 7.20 (m), 6.87 (s), 6.78 (d).

(45) ^1H NMR (CD_2Cl_2) δ 6.51 (q, $J_{PH} = 14$hz), 2.10 (m), 1.54 (m), 1.36 (m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, external H_3PO_4) δ −9.06 (s). IR (CD_2Cl_2) ν(C≡C) 2200 (m) cm^{-1}.

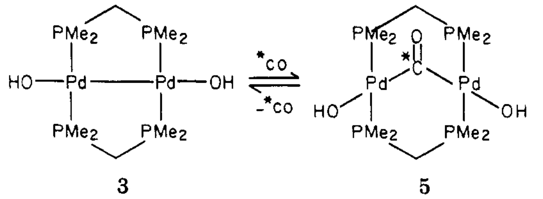
(46) ^1H NMR (CD_2Cl_2) δ 3.28 (m), 1.58 (m), 1.52 (m), (methylene protons are buried under methyl resonances at δ 1.58 and 1.52); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, external H_3PO_4) δ 1.50 (br, s); IR (CH_2Cl_2) ν(CN) 1680 (m), 1635 (s) cm^{-1}.

in D_2O compared to CD_2Cl_2 or CD_3CN reveal little about the differences in identity of 1 in aqueous vs. nonaqueous solvents.[27] However, significant differences in the electronic absorption spectra in aqueous solutions are observed. In H_2O, the UV-vis spectra of 1 exhibits the same features as those seen in CH_2Cl_2 or CH_3CN, but uniformly red-shifted by ~15 nm. The identity of 1 in aqueous solution is largely established by the following set of observations. The addition of $AgBF_4$ to aqueous solutions of 1 leads to precipitation of AgCl and no apparent change in the UV-vis spectrum. This result contrasts strongly to that obtained in CH_3CN solution where spectra obtained before and after AgCl precipitation are markedly different. The addition of Cl^- to aqueous solutions of 1 leads to a blue shift of the spectrum such that in 1 M NaCl the observed UV-vis spectrum is remarkably similar to those obtained in CH_2Cl_2 or CH_3CN solutions without excess chloride. The UV-vis spectra of 1 in H_2O and 1 M aqueous NaCl are presented in Figure 2. Conductivity data suggest that at pH 7, 1 is a neutral complex in H_2O. When 1 is dissolved in aqueous solution, the pH decreases and the solution conductivity increases to a value consistent with a 1:1 electrolyte.[27] These results suggest that liberation of 2 equiv of HCl accompanies dissolution of 1 in H_2O. We note that addition of excess NaCl to aqueous solutions of 1 results in an increase in pH consistent with the reversibility of eq 1. Raman spectra for 1 in H_2O display ν(Pd-Pd) = 140 cm^{-1}, consistent with related Pd-Pd bonded diphosphine-bridged complexes.[40] Raman spectra in H_2O also reveal no bands assignable to ν(Pd-Cl).[40] However, a band at 351 cm^{-1} in H_2O is consistent with ν(Pd-O). These observations collectively point to the identity of 1 in aqueous solution as a neutral, Pd-Pd-bonded binuclear complex, resulting from the substitution of hydroxide for chloride in the positions trans to the Pd-Pd bond, eq 1, to give $Pd_2(OH)_2(dmpm)_2$ (**3**). In an apparently similar reaction, treatment of 1 with 2 equiv of NaOPh leads to $Pd_2(OPh)_2(dmpm)_2$ (**4**).



1 3 (1)

The hydroxide (3) and phenoxide (4) are reactive with respect to the insertion of CO into Pd-Pd and Pd-OR (R = H, Ph) bonds. The treatment of 3 with ^{13}CO in neutral aqueous solution leads initially to Pd-Pd bond insertion, eq 2, to give $Pd_2(OH)_2(\mu\text{-}^{13}CO)(dmpm)_2$.[41] The similarities in ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR data of 2[28] and 5[41] suggest that the aqueous solution structure of 5 is similar to the structurally characterized 2. Significantly, the $^{31}P\{^1H\}$ NMR signal for ^{13}CO-enriched 5 is a first-order doublet (J_{P-C} = 5.4 Hz), consistent with a single bridging CO.



3 5 (2)

Preliminary investigations with the diphenoxide complex (4)[42] suggest that CO insertion into Pd-OPh bonds occurs concurrently with Pd-Pd bond insertion. Spectroscopic data[43] are consistent with the formulation of the product as a diphenyl ester of a dipalladium carboxylic acid, $Pd_2(COPh)_2(\mu\text{-}CO)(dmpm)_2$. Heating the ^{13}CO-enriched diester leads to quantitative evolution of $^{13}CO_2$ and formation of $Pd_2(Ph)_2(\mu\text{-}^{13}CO)(dmpm)_2$.[44] The insertion of CO into the Pd-OR (R = H, Ph) bonds of the new complexes reported herein is the subject of our ongoing investigation. Studies of the insertion of other substrates, notably olefins and acetylenes, into Pd-Pd and Pd-OR are in progress.

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Supplementary Material Available: Positional parameters, temperature factors, bonding and selected nonbonding distances, bond angles, and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

Tetrahedral Mixed-Metal Clusters Containing Bridging Sulfido Ligands. Synthesis and Crystal and Molecular Structures of $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ and $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)$

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Summary: The new tetrahedral mixed-metal cluster compounds $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (**2**) and $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)$ (**4**) have been prepared by the reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ (**1**) with $Pt(PMe_2Ph)_4$ upon mixing at room temperature and with $W(CO)_5(PMe_2Ph)$ in the presence of UV irradiation in yields of 26% and 27%, respectively, and have been characterized by single-crystal X-ray diffraction methods.

Mixed-metal cluster compounds represent an important and rapidly developing new area of transition-metal cluster chemistry.[1] These compounds can serve as intermediates in the synthesis of novel heterogeneous catalysts[2] or as precursors to homogeneous catalysts.[3] Chiral tetranuclear

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