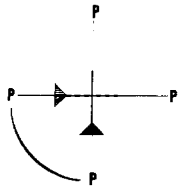
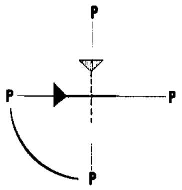
Organometallics **1990**, *9*, 1339–1341

the CO_2 complexes are exposed to $^{13}CO_2$. A reasonable pathway for route ii could involve the intermediacy of an η^1-CO_2 complex[4] of structure A (Scheme I), corresponding to a 16-electron species in which η^1-CO_2 acts as a Lewis acid.[5] This is a very unfavorable electronic situation[6] and, very likely, inaccessible at normal temperatures. Moreover, this mechanism implies the inequivalence of the two CO_2 ligands in compounds **2** in the high-temperature limit, in disagreement with the observation of a single resonance (triplet of doublets, $^2J(CP_1) \simeq 20$ Hz, $^2J(CP_2) \simeq 10$ Hz) in their $^{13}C\{^1H\}$ NMR spectra.[1]

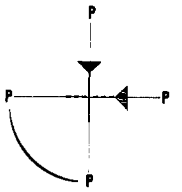
For compounds **3**, the three different rotamers B–D (and their corresponding enantiomers) can exist, and they are indeed observed in the low-temperature (−80 °C, 81 MHz) $^{31}P\{^1H\}$ NMR spectrum of **3a**. At higher temperatures, interconversion of the isomers is fast on the NMR time scale, as shown by the observation of an AA′XX′ pattern in the fast exchange limit (60 °C, 81 MHz). Since the independent rotation would involve at some stage a transition state or intermediate that would introduce an effective plane of symmetry, the observation of two different resonances for the methyl groups of the chelating diphosphine ligands in the ^1H NMR spectra of **3a** and **3c** recorded at 60 °C clearly argues against this pathway.



B

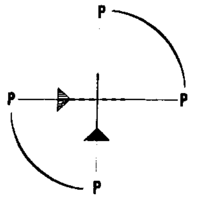


C

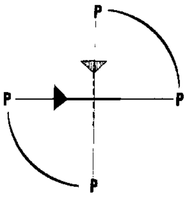


D

Similar observations with reference to compounds **4** can be used to discard the disrotatory motion (pathway v). Two rotamers, E and F, can exist for these complexes, and indeed both can be detected by ^{31}P NMR spectroscopy. Thus, the $^{31}P\{^1H\}$ NMR spectra of **4a** and **4b** show, at −20 °C, two AA′XX′ patterns assigned to the corresponding rotamers with structures E and F. At 20 °C, these sets of resonances convert into two very broad features that give rise to a broad singlet ($\Delta\nu \simeq 14$ Hz) at 110 °C (toluene) and finally transform into a sharp singlet ($\Delta\nu \simeq 3$–4 Hz) at 150 °C in mesitylene. Therefore, in the high-temperature limit, fast interconversion of rotamers E and F takes place. This is in disagreement with the disrotatory movement but is in excellent accord with the conrotatory mechanism, since the former would convert rotamer E into itself or its enantiomer (consider, for example, a 360° rotation of the CO_2 ligands, carried out in four 90° steps) while the latter interconverts rotamers E and F. At variance with the disrotatory motion, which would proceed through transition states or intermediates that possess either an effective plane of symmetry containing the MoP_4 unit or a center of inversion, the interconversion of E and F by the conrotatory mechanism does not introduce any additional elements of symmetry. Hence, two resonances are expected for the methyl protons of the diphosphine ligands of compound **4a** in the fast exchange limit, in excellent agreement with the experimental results.



E



F

In conclusion, we have convincingly demonstrated the existence of rotational isomerism in $(CO_2)_2$ adducts, *trans*-$[Mo(CO_2)_2L_xL'_{4-x}]$, and shown that the observed rotamers interconvert by a concerted motion of the CO_2 ligands in which both molecules of carbon dioxide rotate synchronously in the same direction. These experimental observations are in accord with recent theoretical calculations by Sânchez-Marcos et al. that had predicted this behavior. This study concluded[7] that the more stable conformations have the CO_2 ligands mutually perpendicular while the conformers with eclipsed CO_2 groups have much higher energies (about 70 kcal mol^{-1}). Finally, since the conrotatory motion of the CO_2 ligands does not interchange enantiomeric structures, the isolation of optically active carbon dioxide complexes of this type seems feasible. Work aimed at this purpose is currently under way in our laboratory.

Acknowledgment. We thank the Dirección General de Política Científica for financial support.

Supplementary Material Available: Representative variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectra of complexes **3a**, **3c**, and **4a** (3 pages). Ordering information is given on any current masthead page.

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[4] As pointed out by one reviewer, the exchange of the free and coordinated oxygen atoms of the CO_2 ligands does not necessarily require the intermediacy of an η^1-CO_2 complex. It should be noted, however, that the nature of the intermediate or transition state associated with this mechanism does not alter the conclusions reached with respect to its feasibility.

[5] Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983**, *103*, 5914.

[6] Mealli, C.; Hoffmann, R.; Stockis, A. *Inorg. Chem.* **1984**, *23*, 56.

[7] Sânchez-Marcos, E.; Caballol, R. Trinquier, G.; Bartherlat, J. C. *J. Chem. Soc., Dalton Trans.* **1987**, 2373.

Ligand Influences on the State of Cluster Aggregation. Ligand-Dependent Formation of Cluster Complexes with $[PtRu_2]_n$ (n = 1–3) Metal Groupings

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Received January 29, 1990

Summary: The reaction of $Pt(COD)_2$ with $Ru(CO)_5$ at 25 °C produced the hexanuclear metal complex $[PtRu_2(CO)_9]_2$ (**1**) in 31% yield, which consists of an open cluster containing two ruthenium atoms bonded to two platinum atoms followed by two additional ruthenium atoms. Compound **1** reacted with dppe by a symmetrical cleavage of the molecule to yield $PtRu_2(CO)_8(dppe)$ (**2**). The reaction of **1** with PhC_2Ph produced the higher cluster $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}PhC_2Ph)_3$ (**3**) in 30% yield. Compound **3** consists of a Pt_3Ru_3 octahedron with three ruthenium atoms capping triangular faces. It also contains three triply bridging PhC_2Ph ligands.

In recent studies, we have demonstrated the effects of bridging sulfido ligands on promoting the agglomeration[1]

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[1] (a) Adams, R. D.; Babin, J. E.; Wolfe, T. A. *Polyhedron* **1989**, *8*, 1123. (b) Adams, R. D.; Mannig, D.; Segmüller, B. E. *Organometallics* **1983**, *2*, 149. (c) Adams, R. D.; Hor, T. S. A. *Organometallics* **1984**, *3*, 1915.

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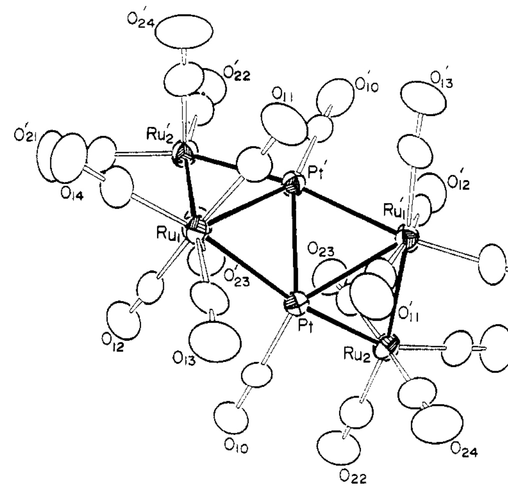

Figure 1. ORTEP diagram of $[PtRu_2(CO)_9]_2$ (1) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å) are Pt–Pt′ = 2.6656 (8), Pt–Ru(1) = 2.8730 (8), Pt–Ru(2) = 2.6456 (8), and Pt′–Ru(1) = 2.8160 (8).

and condensation[2] of metal carbonyl cluster complexes. We have now found that the reaction of $Pt(COD)_2$ (COD = 1,5-cyclooctadiene) with $Ru(CO)_5$ leads to the formation of the novel mixed-metal cluster complex $[PtRu_2(CO)_9]_2$ (1), which can be viewed as a dimer of the unknown and unsaturated parent $[PtRu_2(CO)_9]$. Upon reaction with suitable ligands the dimer 1 can be split, or split and reassembled to form a higher nuclearity species derived from the condensation of three $PtRu_2$ groupings.

The reaction of $Pt(COD)_2$ with $Ru(CO)_5$ proceeds smoothly at 25 °C in hexane solvent to yield the new complex $[PtRu_2(CO)_9]_2$ (1) in 31% yield.[3] Compound 1 was characterized by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 1.[4,5] The molecule contains an open, but folded, array of six metal atoms. Two mutually bonded ruthenium atoms, Ru(1)–Ru(2′) = 2.8480 (9) Å, are joined to the two mutually bonded platinum atoms, Pt–Pt′ = 2.6656 (8) Å, which are bonded to a second pair of mutually bonded ruthenium atoms, Ru(2)–Ru(1′). The molecule contains a crystallographically imposed 2-fold rotation axis that lies perpendicular to the Pt–Pt′ and Ru(1)···Ru(1′) vectors. Ru(1) and Ru(1′) are bonded to Ru(2′) and Ru(2), respectively, and to both platinum atoms, but they are not bonded to each other. Ru(2) and Ru(2′) are bonded only to one ruthenium atom and one platinum atom. The Ru–Pt bond distances to Ru(1) are significantly different, Pt–Ru(1) = 2.8730 (8) Å and Pt′–Ru(1) = 2.8160 (8) Å, and both are significantly longer than the Pt–Ru(2) distance, 2.6456 (8) Å. Each ruthenium atom contains four terminal carbonyl ligands. The metal–metal bonding in **1** is very unusual. Ru(2) and Ru(2′) both achieve 18-electron configurations by deriving one electron from each metal–metal bond and eight electrons from their four CO ligands. Ru(1) could achieve an 18-electron configuration by deriving one electron from the bonds to Ru(2′) and Pt′ and eight electrons from its four CO ligands. The remaining long Ru(1)–Pt bond could be regarded as a weak donor/acceptor bond from Ru(1) to Pt. The short Pt–Pt′ distance is indicative of a significant bonding interaction. A molecular orbital description of the bonding in 1 is currently being developed.[6]

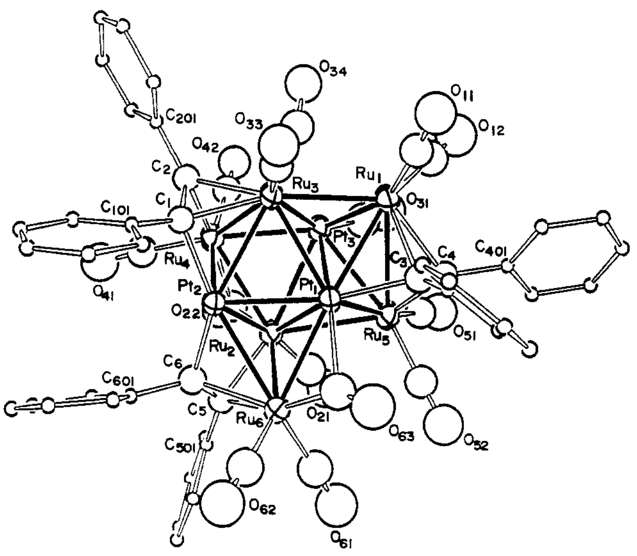

Figure 2. ORTEP drawing of $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}PhC_2Ph)_3$ (3) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å) are Pt(1)–Ru(1) = 2.699 (2), Pt(1)–Pt(2) = 2.702 (1), Pt(1)–Ru(3) = 2.714 (2), Pt(1)–Ru(6) = 2.785, Pt(1)–Ru(2) = 2.937 (2), Pt(2)–Ru(2) = 2.667 (2), Pt(2)–Ru(4) = 2.719 (2), Pt(2)–Ru(3) = 2.760 (2), Pt(2)–Ru(6) = 2.817 (2), Pt(3)–Ru(1) = 2.648 (2), Pt(3)–Ru(4) = 2.685 (2), Pt(3)–Ru(3) = 2.716 (2), Pt(3)–Ru(5) = 2.721 (2), Pt(3)–Ru(2) = 2.817 (2), Ru(1)–Ru(3) = 2.730 (2), Ru(2)–Ru(4) = 2.757 (2), Ru(2)–Ru(6) = 2.788 (2), Ru(2)–Ru(6) = 2.920 (2), Ru(3)–Ru(4) = 2.782 (2), Pt(1)–Pt(3) = 3.124 (1), Ru(1)–Ru(5) = 3.125 (2).

Compound 1 engages in reactions which suggest that a facile and symmetrical splitting of the molecule can occur. When 1 was treated with 1,2-bis(diphenylphosphino)ethane (dppe), the known trinuclear cluster complex $Ru_2Pt(CO)_8(dppe)$ (2) was formed in good yield.[7,8] When 1 was treated with PhC≡CPh, the new complex $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}PhC_2Ph)_3$ (3) was formed in 30% yield.[9] An ORTEP drawing of the molecular structure of 3 is shown in Figure 2.[5,10] The cluster contains three platinum and six ruthenium atoms and could be described as a tricapped

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[2] (a) Adams, R. D.; Dawoodii, Z.; Foust, D F.; Segmüller, B. E. *J. Am. Chem. Soc.* **1983**, *105*, 831. (b) Adams, R. D. *Polyhedron* **1985**, *4*, 2003. (c) Adams, R. D.; Wang, J. G. *Polyhedron* **1989**, *11*, 1437. (d) Adams, R. D.; Chen, G.; Tanner, J. T.; Yin, J. *Organometallics*, in press.

[3] Compound 1 was isolated by TLC on silica gel by elution with a hexane/CH_2Cl_2 (95/5) solvent mixture. For 1: IR (ν(CO), cm^{-1}, in hexane) 2085 (m), 2062 (vs), 2035 (s), 2016 (w). Satisfactory elemental analyses for C and H have been obtained.

[4] Crystals of 1 were grown by slow evaporation of solvent from hexane solutions at 5 °C: space group $C2/c$, a = 12.542 (2) Å, b = 15.350 (4) Å, c = 15.252 (3) Å, β = 105.32 (2)°, Z = 4. An empirical absorption correction was applied to the data. The structure was solved by direct methods and was refined (2192 reflections) to the final residuals R = 0.025 and R_w = 0.030.

[5] Diffraction measurements were made on a Rigaku AFC6S diffractometer using Mo Kα radiation. Calculations were performed on a Digital Equipment Corp. MICROVAX II computer by using the TEXSAN structure solving program library obtained from Molecular Structure Corp., The Woodlands, TX.

[6] Adams, R. D.; Chen, G.; Hoffmann, R.; Proserpio, D. M.; Wang, J. G.; Wu, W. Studies in progress.

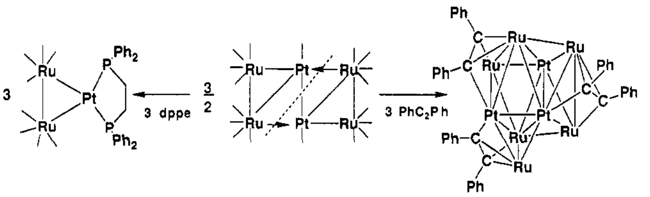
[7] The reaction of 1 with dppe proceeded at 0 °C in CH_2Cl_2 solvent to give a 47% yield of 2 in a period of 65 min. Compound 2 is spectroscopically identical with the product having the same formula that was prepared by Bruce et al.[8]

[8] Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1781.

[9] The reaction of 1 with PhC_2Ph was carried out in refluxing heptane solvent. The compound was isolated as a dark green band by TLC on silica gel with a hexane/CH_2Cl_2 (7/3) elution solvent. IR (ν(CO), cm^{-1}, in hexane): 2058 (m), 2040 (vs), 2024 (s), 2018 (s), 2001 (s), 1979 (w), 1970 (w), 1962 (w), 1944 (w), 1897 (w), 1886 (sh). ^1H NMR (δ, in $CDCl_3$): 6.2–8.0 (Ph). Satisfactory elemental analyses for C and H have been obtained.

[10] Crystals of 3 were grown from hexane solutions at 10 °C: space group $P\bar{1}$, a = 15.218 (2) Å, b = 15.444 (3) Å, c = 14.464 (3) Å, α = 94.48 (2)°, β = 100.29 (1)°, γ = 87.55 (2)°, z = 2. An empirical absorption correction was applied. The structure was solved by direct methods and was refined (4722 reflections) to the final residuals R = 0.040 and R_w = 0.040; 1.5 formula equiv of C_6H_{14} was found to have cocrystallized in the crystal lattice with 3.

Scheme I



(Ru(1), Ru(5), Ru(6)) octahedron (Ru(2), Ru(3), Ru(4), Pt(1), Pt(2), Pt(3)) with a bond between the capping atoms Ru(1) and Ru(5). With 22 metal-metal bonds, 18-electron configurations can be assigned to each metal atom, although some of the metal-metal bonds (e.g. Ru(3)-Ru(1)) must be viewed formally as donor/acceptor bonds. Two of the metal-metal bonds are unusually long, Ru(1)-Ru(5) = 3.125 (2) Å and Pt(1)-Pt(3) = 3.124 (1) Å, but bonds of similar lengths have been observed in other platinum[11] and ruthenium[2d] cluster complexes. Compound **3** contains three triply bridging PhC_2Ph ligands that occupy triangular $PtRu_2$ groupings and 14 carbonyl ligands. The molecule could be viewed as an assembly derived from three $PtRu_2(\mu_3\text{-}PhC_2Ph)$ groupings, although details of the mechanism of formation are not available at this time. Both the dppe and PhC_2Ph reactions with **1** suggest that a splitting of **1** to $PtRu_2$ groupings is occurring. With dppe, the $PtRu_2$ grouping is stabilized, and the complex **2** is isolable. With PhC_2Ph three $PtRu_2$ groups condense to **3** (see Scheme I). In the presence of carbonyl ligands only, the dimer **1** is the most stable form of the complex.

It has been proposed that the series of oligomeric platinum cluster complexes $[Pt_3(CO)_6]_n^{2-}$ (n = 2-5)[11] interconvert by the transfer of unsaturated "$Pt_3(CO)_6$" groupings.[12] As illustrated by the reactions of **1**, this behavior may extend to other platinum-containing cluster complexes and may be influenced and possibly controlled by the ligands.

Acknowledgment. These studies were supported by the National Science Foundation under Grant CHE8919786.

Supplementary Material Available: Tables of crystal data, positional and anisotropic thermal parameters, and bond distances and angles for the structural analysis of compounds **1** and **3** (25 pages); tables of structure factor amplitudes (47 pages). Ordering information is given on any current masthead page.

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(11) Calabrese, J. C.; Dahl, L. F.; Chini, P.; Longoni, G.; Martinengo, S. *J. Am. Chem. Soc.* **1974**, *96*, 2614.

(12) (a) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37. (b) Brown, C.; Heaton, B. T.; Towl, A. D. C.; Longoni, G.; Fumagalli, A.; Chini, P. *J. Organomet. Chem.* **1979**, *181*, 233.

Synthesis and Characterization of Monooxo Alkyl Complexes of Ruthenium(VI) and Osmium(VI)

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Received December 6, 1989

Summary: Monooxo alkyl complexes of osmium(VI) and ruthenium(VI) with the molecular formula $M(O)(CH_2SiMe_3)_4$ have been synthesized from ((trimethylsilyl)methyl)magnesium compounds and $[PPh_4]_2[Os(O)_2Cl_4]$, $[PPN]_2[Ru(O)_2Cl_4]$, or $[PPh_4]_2[Os(O)_2(OSiMe_3)_4]$. The complexes were characterized by IR, NMR, and UV-visible spectroscopy and electrochemistry. The molecular structure of $Os(O)(CH_2SiMe_3)_4$ was determined by single-crystal X-ray diffraction.

Transition-metal oxo complexes are important for their properties as materials, as catalysts and reagents for oxidation reactions, and as models for certain metalloenzymes (cytochrome P450, isopenicillin N synthase). Because of this, activity on the synthesis, structure, and reaction chemistry of oxo complexes has increased dramatically in recent years.[1]

In order to directly compare the effects of multiply bonded ligands on a metal, it is necessary to prepare isoelectronic and isostructural complexes containing oxo, nitrido, and alkylimido groups. We have previously prepared alkyl complexes of ruthenium(VI) and osmium(VI) that contain terminal nitrido or alkylimido ligands.[2] These complexes have the formula $[M(N)R_4]^-$ and $M(NR')R_4$. The osmium complexes $[NBu^n{}_4][Os(N)(CH_2SiMe_3)_4]$ and $Os(NMe)(CH_2SiMe_3)_4$ were structurally characterized.[3] An isoelectronic oxo complex, $Os(O)(CH_2SiMe_3)_4$, was reported by Wilkinson and co-workers.[4] The oxo compound was prepared in 12% yield by the direct reaction of bis((trimethylsilyl)methyl)magnesium with osmium tetroxide. The ruthenium analogue cannot be prepared by this route, however. As part of our study of the reactivity of high-oxidation-state organometallic complexes, we sought to develop a more general synthetic route to the osmium and ruthenium oxo alkyl complexes $M(O)R_4$. Here we report the synthesis and characterization of $Os(O)(CH_2SiMe_3)_4$ and $Ru(O)(CH_2SiMe_3)_4$ and the structure of the osmium complex by single-crystal X-ray diffraction.

A number of inorganic oxo complexes of ruthenium and osmium in the +6 oxidation state have been prepared, but most of these are inappropriate precursors to oxoalkylmetal complexes since they are insoluble in nonprotic solvents and are easily reduced.[5] The tetraphenylphosphonium and bis(triphenylphosphine)nitrogen(1+) salts of the dioxometal tetrachlorides, $[PPh_4]_2[Os(O)_2Cl_4]$[6] and $[PPN]_2[Ru(O)_2Cl_4]$,[7] are moderately soluble in dichloromethane. More soluble complexes can be prepared by metathesis of the chloride ligands for trimethylsiloxide. Treatment of $[PPh_4]_2[Os(O)_2Cl_4]$ with 4 equiv of sodium trimethylsiloxide in dichloromethane produced $[PPh_4]_2[Os(O)_2(OSiMe_3)_4]$ in good yield. Analytically pure ma-

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(1) For a review of recent research on metal oxo complexes see: Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(2) (a) Belmonte, P. A.; Own, Z.-Y. *J. Am. Chem. Soc.* **1984**, *106*, 7493-6. (b) Shapley, P. A.; Wepsiec, J. P.; *Organometallics* **1986**, *5*, 1515-7. (c) Shapley, P. A.; Kim, H. S.; Wilson, S. R. *Organometallics* **1988**, *7*, 928-33.

(3) Shapley, P. A.; Own, Z.-Y.; Huffman, J. C. *Organometallics* **1986**, *5*, 1269-71.

(4) Alves, A. S.; Moore, D. S.; Andersen, R. A.; Wilkinson, G. *Polyhedron* **1982**, *1*, 83-7.

(5) (a) Wintrebert, L. *Ann. Chim. Phys., Ser. VII* **1903**, *28*, 45-96. (b) Hepworth, M. A.; Robinson, P. L. *J. Inorg. Nucl. Chem.* **1957**, *4*, 24-29. (c) Colton, R.; Farthing, R. H. *Aust. J. Chem.* **1968**, *21*, 589-93. (d) Bol'shakov, K. A.; Sinitsyn, N. M.; Bodnar', N. M.; Danilov, S. R. *Dokl. Chem. (Engl. Transl.)* **1972**, *206*, 772-5. (e) Bol'shakov, K. A.; Sinitsyn, N. M.; Bodnar', N. M.; Bordat, V. F.; Sineshchekova. *Dokl. Akad. Nauk SSSR* **1973**, *210*, 1396-9.

(6) A solution of $[OsO_2Cl_4]^{2-}$ was prepared by dissolving potassium osmate, $K_2[Os(O)_2(OH)_4]$ (0.229 g, 0.622 mmol), in 50 mL of 2 M HCl. Addition of PPh_4Cl (0.7 g in 45 mL of 2 M HCl) caused immediate precipitation of the buff-colored product $[PPh_4]_2[OsO_2Cl_4]$ in 87% yield. ^1H NMR (CD_2Cl_2, 300 MHz, 19 °C): δ 7.69 (m, 2 H, *o*-H), 7.78 (m, 2 H, *m*-H), 7.89 (m, 1 H, *p*-H). IR (KBr, cm^{-1}): 840 s (OsO_2). Anal. Calcd for $C_{48}H_{40}Cl_4OsO_2P_2$: C, 55.28; H, 3.86. Found: C, 55.09; H, 3.83.

(7) Kochi, J. K.; Perrier, S. *Inorg. Chem.* **1988**, *27*, 4165-73.

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