The characterization data are consistent with the formulation of **3** as the carbonyl adduct of **1** with one CO ligand bonded to the Pd atom. This reaction is analogous to the reaction of $[Au_8Pt(PPh_3)_8](NO_3)_2$ with CO, which yielded $[Au_8Pt(PPh_3)_8(CO)](NO_3)_2$.[6] The $^{31}P\{^1H\}$ NMR spectrum (CH_2Cl_2, 25 °C) of **3** showed a single resonance at δ 44.5 (singlet). The ^{13}C NMR solution spectrum (CD_2Cl_2, 25 °C) of isotopically labeled $[Au_8Pd(PPh_3)_8(^{13}CO)](NO_3)_2$ complex consisted of a multiplet of seven well-resolved lines not inconsistent with a nonet pattern where the wing resonances are in the noise centered at δ 229.7 ($J_{^{13}C-P}$ = 11.7 Hz). The IR spectrum (KBr) of **3** displayed a ν(CO) absorption at 1955 cm^{-1}, which is consistent with a terminally bound metal carbonyl. The ν(CO) absorption shifted to lower energy (1919 cm^{-1}) in the IR spectrum when **3** was synthesized with 99% ^{13}CO. The conductance of **3** in CH_3CN showed it to be a 1:2 electrolyte.

Preliminary results indicate that this class of cluster compounds possesses a rich chemistry. We are presently studying these complexes with respect to their catalytic potential, their reactivity with small molecules, and their reactivity with other transition-metal cations in an attempt to synthesize trimetallic clusters. For example, in addition to the reaction with CO, we have discovered that complex **1** reacts with MeI and $AgNO_3$.

Acknowledgment. This work was supported by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Experimental details of the X-ray structure determination, Figures S1 and S2, displaying PLUTO drawings (two views) of **1**, and Tables I–VI, listing crystal structure data collection and refinement parameters, final positional and thermal parameters for all atoms including calculated hydrogen positions, distances and angles, least-squares planes, and general temperature factor expressions (27 pages); Table VII, listing observed and calculated structure factor amplitudes (54 pages). Ordering information is given on any current masthead page.

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(31) $[Au_8Pd(PPh_3)_8(CO)](NO_3)_2$ (**3**) was prepared by dissolving complex **1** (100 mg, 2.56×10^{-2} mmol) in 10 mL of dichloromethane and placing the solution under 1 atm of CO. The color of the solution changed from purple to dark brown immediately. The volume of the solution was reduced to 2 mL and transferred to a flask containing 60 mL of diethyl ether. The brown precipitate was collected on a fritted filter, washed with 40 mL of diethyl ether, and dried under vacuum. Yield: 98 mg (97%). It is soluble in alcohols, dichloromethane, chloroform, and acetone and insoluble in saturated hydrocarbons and diethyl ether; it is air-, light-, and moisture-stable both in the solid state and in solution. The isotopically labeled analogue, $[Au_8Pd(PPh_3)_8(^{13}CO)](NO_3)_2$, was prepared by the same procedure using ^{13}CO.

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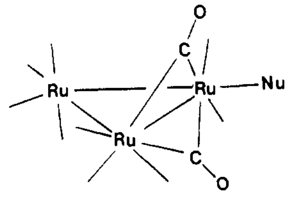
Nucleophilic Activation of Metal Carbonyl Clusters.[1] Isolation and Structure of the Elusive Chloride Adduct $Ru_3(CO)_{11}Cl^-$

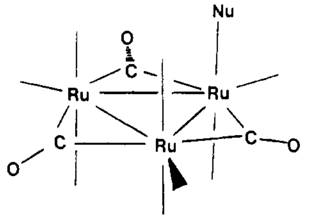
Homogeneous catalysts based on metal carbonyls often employ anionic nucleophile promoters;[2] e.g., halides are used as promoters in catalysis by the prototype cluster $Ru_3(CO)_{12}$.[3,4] While the roles of such promoters are yet to be fully delineated, Kaesz,[5] Gladfelter,[6] and others[7] have shown facile nucleophilic attack of halides and other anions on $Ru_3(CO)_{12}$ in certain media to result in CO labilization to give anionic clusters $Ru_3(CO)_mX_n^{n-}$. Recently, Han et al.[8] described reversible transformations for some products from reactions of $Ru_3(CO)_{12}$ plus the salts [PPN]Nu ($PPN^+ = (Ph_3P)_2N^+$; $Nu^- = Cl^-, Br^-, I^-$) in tetrahydrofuran. On the basis of in situ spectroscopic evidence, the initial cluster product with Cl^- (eq 1) was proposed to have the stoichiometry $Ru_3(CO)_{11}Cl^-$

$$Ru_3(CO)_{12} + Cl^- \rightarrow Ru_3(CO)_{11}Cl^- + CO \qquad (1)$$

and a structure such as illustrated by A. However, attempts to isolate this anionic cluster[8] or analogous triruthenium products with other anions[6,7c] have been frustrated by the apparent instability of the $Ru_3(CO)_{11}Nu^-$ species. Described here is the successful isolation and structural characterization of one example of this key intermediate, the unstable salt $[PPN][Ru_3(CO)_{11}Cl]$ (I). In this case the cluster anion is shown to have the configuration B, different from that proposed.



A



B

A solution of I was prepared by adding 10 mL of deaerated THF to a nearly equimolar mixture of the two solids [PPN]Cl (0.062 g, 0.10 mmol) and $Ru_3(CO)_{12}$ (0.058 g, 0.09 mmol) under CO in a Schlenk tube. After 30 min of stirring, all the solid had dissolved and the initially orange solution had turned to a deep red color. The THF was then removed by evaporation under vacuum to leave a dark red solid residue. A CO atmosphere was reintroduced into the Schlenk tube, and a minimal amount of diethyl ether was added (under CO) to redissolve the solid. The resulting dark red solution was then transferred via syringe and under CO to the inner chamber of a special Schlenk tube modified for recrystallization via the solvent vapor-exchange method.[9] Hexane, deaerated by entraining with CO, was added via syringe to the outer chamber of the same apparatus, and the system was left undisturbed for several hours while dark red crystals formed with size and quality suitable for single-crystal X-ray structure determination. The elemental analysis of the recrystallized adduct was shown to be consistent with the formulation $[PPN][Ru_3(CO)_{11}Cl]$.[10]

The FTIR spectrum of I when redissolved in THF under CO gave ν_{CO} bands at 2060 s, 2026 vs, 2009 s, 1975 m, 1962 m, and 1828 s, br cm^{-1}. The only substantive difference between this

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(1) Reported initially at the 196th National Meeting of the American Chemical Society, Los Angeles, CA, Sept 1988.

(2) Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139–217 and references therein.

(3) (a) Dombek, B. D. *Organometallics* **1985**, *4*, 1707–1712 and references therein. (b) Knifton, J. F. *J. Mol. Catal.* **1981**, *11*, 91–106. (c) Hidai, M.; Koyasu, Y.; Chikanari, K.; Uchida, Y. *J. Mol. Catal.* **1987**, *40*, 243–254.

(4) (a) Zuffa, J. L.; Blohm, M. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 552–553. (b) Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; La Monica, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1286–1287. (c) Yoshida, S.-I.; Mori, S.; Kinoshita, H.; Watanabe, Y. *J. Mol. Catal.* **1987**, *42*, 215–227.

(5) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647–4648.

(6) (a) Fjare, D. E.; Jensen, J. A.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 1774–1780. (b) Stevens, R. E.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 2034–2042.

(7) (a) Rokicki, A.; Taube, D.; Ford, P. C. Presented at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, Sept 1986. (b) Sailor, M. J.; Brock, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 6015–6022. (c) Lavigne, G.; Lugan, N.; Bonnet, J.-J. *J. Chem. Soc., Chem. Commun.* **1987**, 957–958.

(8) Han, S.-H.; Geoffroy, G. L.; Dombek, B. D.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 4355–4361.

(9) Friedman, A. E.; Ford, P. C. In *Experimental Organometallic Chemistry, A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; pp 68–69.

(10) Elemental analysis was performed by Galbraith Laboratories. Calcd for $C_{47}H_{30}O_{11}NP_2ClRu_3$: C, 47.62; H, 2.55; N, 1.18; Cl, 2.99. Found: C, 46.60; H, 2.64; N, 1.14; Cl, 2.99.

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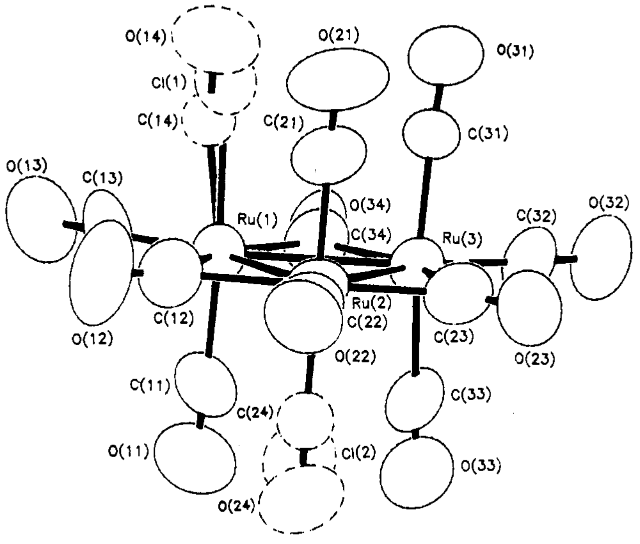

Figure 1. Structure of the $Ru_3(CO)_{11}Cl^-$ ion, showing the disorder of the chlorine atom between the Cl(1) and Cl(2) positions. In this representation, the PPN^+ cation lies below the Ru_3 plane.

spectrum and one of the solid salt in a Nujol mull was a shift of the lowest frequency band to 1815 cm^{-1}. These spectral properties agree with earlier in situ observations.[7b,8] The UV/vis spectrum of I in CO-saturated THF gave a broad shoulder with λ_{max} at 404 nm ($\epsilon = 5 \times 10^3$ M^{-1} cm^{-1}). Flushing the solution with N_2 led to a shift in the spectrum to give a new band at λ_{max} = 324 nm consistent with the reversible dissociation of CO to give $Ru_3(CO)_{10}Cl^-$ under these conditions.[7a,8]

The conformation of the cluster anion $Ru_3(CO)_{11}Cl^-$ is shown in Figure 1.[11] Key bond lengths and bond angles are listed in Table 1 (supplementary material). The most serious problem in solving this structure was a disorder such that the Cl atom has about equal population in axial positions on two different Ru's related to each other by a 180° rotation about an axis lying in the Ru_3 plane and bisecting the Ru–Ru bond. This disorder problem was solved by assigning 50% occupancy to the chloride and carbonyl groups CO(14) and CO(24) and restraining the distances Ru(1)–C(14) and Ru(2)–C(24) to 1.95 (1) Å and C(14)–O(14) and C(24)–O(24) to 1.125 (1) Å and then allowing the structure to refine by successive cycles of least-squares refinement. The final occupancies for chlorine in the Cl(1) and Cl(2) positions were determined by least-squares refinement to be 49.9 and 50.1%, respectively.

From Figure 1 it is seen that the structure of $Ru_3(CO)_{11}Cl^-$ consists of a triangle of Ru atoms with six carbonyls, three bridging and three terminal, lying in equatorial positions relative to Ru_3. The Ru(1)–Ru(2), Ru(1)–Ru(3), and Ru(2)–Ru(3) bond lengths are respectively 2.868 (1), 2.854 (1), and 2.869 (2) Å. The disordered chlorine atom and five carbonyls are in axial positions. The angles between the three planes defined by C(12), C(23), and C(34) with the respective two ruthenium atoms they bridge and the plane defined by the Ru_3 triangle are in each case greater than 178°. Notably, the orientation of the equatorial carbonyls is quite analogous to that reported[7c] for each Ru_3 unit of the dimer $[Ru_3(CO)_{10}CN]_2^{2-}$, which is linked by two axial CN's bridging the triangular cluster units.[12]

Preliminary kinetics studies in this laboratory have demonstrated that, in a THF/CH_2Cl_2 mixed solvent, eq 1 occurs at a rate orders of magnitude faster than those for the analogous substitutions with neutral phosphines as the attacking ligand.[13] The rates are dependent on $[PPN^+Cl^-]$ but essentially independent of P_{CO}; thus, nucleophilic attack of Cl^- on the $Ru_3(CO)_{12}$ cluster is the apparent rate-limiting step of this activation mechanism. Kinetic studies in progress are attempting to differentate whether the initial site of Cl^- attack occurs at one of the carbonyls to give the species $Ru_3(CO)_{11}(C(O)Nu)^-$ (as has been observed[14] with oxygen bases such as CH_3O^- and proposed[15] to be the case with halide nucleophiles) or occurs directly at one of the metal centers.

Acknowledgment. Dr. Andrzej Rokicki performed many of the preliminary experiments involved with characterizing the reactions of [PPN]Cl with $Ru_3(CO)_{12}$. This research was supported by a grant (No. DE-FG03-85ER13317) from the Division of Chemical Sciences, Office of Basic Energy Science, U.S. Department of Energy.

Supplementary Material Available: Tables 1–3, listing selected bond lengths and angles for the anion $Ru_3(CO)_{11}Cl^-$ and positional parameters for all non-hydrogen atoms and cell constants and crystallographic data for $[PPN][Ru_3(CO)_{11}Cl]$, and Figure 2, showing a view of the unit cell of $[PPN][Ru_3(CO)_{11}Cl]$ (5 pages). Ordering information is given on any current masthead page.

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(11) (a) Crystal data: The compound $[PPN][Ru_3(CO)_{11}Cl]$ crystallizes in the triclinic system, space group $P\bar{1}$, with a = 9.137 (2) Å, b = 14.397(3) Å, c = 19.226(4) Å, α = 69.34 (5)°, β = 89.76 (5)°, γ = 86.38 (5)°, V = 2361.3 Å^3, Z = 2, and ρ_{calcd} = 1.67 g/cm^3. A Huber automated four-circle diffractometer interfaced to a DEC micro-VAX II computer with stepping motor controllers from Crystal Logic was used to obtain the diffraction data. Data were collected at 298 K with Mo Kα radiation (λ = 0.710 69 Å) between 2θ = 0 and 50°. The data were collected in three shells, and data reduction was performed by using the program CARESS of the UCLA computing package. With the use of 3545 observed ($I > 5\sigma(I)$) reflections, the structure was solved by direct methods using SHELXS-86 and the remaining non-hydrogen atoms were located by using difference Fourier syntheses after refinement of the known atom positions. All the least-squares and subsidiary calculations were performed by using the Oxford CRYSTALS system (ref 11b). The current $R(R_w)$ values are 4.91% (2.77%). The weighting scheme used was that of Tukey and Prince,[11c] such that $w = w'[(1 - (\Delta(F)/6(\sigma F)_{est})^2]^2$, with w' described by a three-term Chebychev polynomial[11d] with coefficients determined by least-squares fit. Outliers are down weighted by this scheme; hence, R_w is somewhat smaller than R. R_w for unit weights is 4.90%. We have not specified the error of fit, S, due to uncertainties in assigning correct weights to the reflection data.[11e] (b) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. "CRYSTALS User Guide", Chemical Crystallography Laboratory, Oxford University, 1985. (c) Prince, E. *Mathematical Techniques in Crystallography*; Springer-Verlag: New York, 1982. (d) Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr.* **1979**, *A35*, 698. (e) Watkin, D. J. Personal communication.

(12) (a) Recently, Gladfelter et al.[12b] accomplished the single-crystal X-ray crystallographic analysis of the PPN^+ salts of the osmium carbonyl anions $Os_3(CO)_{11}Br^-$ and $Os_3(CO)_{11}I^-$. In both cases, all the carbonyls are terminal, but the Br^- adduct has the bromine atom in an axial site, while the I^- adduct has the iodine atom in an equatorial site. NMR studies indicate that the structures of the Cl^- and NCO^- adducts are analogous to that of the Br^- adduct. (b) Zuffa, J. L.; Kivi, S. J.; Gladfelter, W. L. Submitted for publication (private communication from Wayne Gladfelter).

(13) (a) Poë, A.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860–1866. (b) The rates of phosphine reaction with $Ru_3(CO)_{12}$ described in ref 12a were measured in nonpolar hydrocarbon solvents. The kinetics of similar reactions in THF were probed in this laboratory[13c] and found to be analogously slow. (c) Chin-Choy, T. Ph.D. Dissertation, University of California, Santa Barbara, 1989.

(14) Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 585–593.

(15) (a) Lavigne, G.; Kaesz, H. D. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knözinger, H., Eds.; Elsevier Science Publishers: Amsterdam, 1986; pp 67–69. (b) These authors[15a] also postulated another possible structure for the $Ru_3(CO)_{11}Nu^-$ adduct formed from reaction of $Ru_3(CO)_{12}$ with an anionic nucleophile Nu^-. In this structure Nu^- occupies an axial site and the all the CO's are terminally bound, analogous to the structure recently determined for $Os_3(CO)_{11}Br^-$.[12]

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