J|A|C|S
COMMUNICATIONS

Lewis Acid−Base Interactions between Metal Atoms and Their Applications for the Synthesis of Bimetallic Cluster Complexes

Richard D. Adams,* Burjor Captain, Wei Fu, and Mark D. Smith
Department of Chemistry and Biochemistry, University of South Carolina Columbia, South Carolina 29208

Received November 7, 2001

Metal complexes can serve as donors in Lewis acid−base adduct formation.[1,2] The basicity of the metal−metal bonds of polynuclear metal complexes toward protons has also been investigated.[3] Here we report on the remarkable ability of ruthenium−ruthenium bonds to engage in a novel adduct formation to the Lewis acid palladium grouping $\mathrm{Pd(PBu^t{}_3)}$.

The tripalladium complex $\mathrm{Ru_3(CO)_{12}[Pd(PBu^t{}_3)]_3}$ **1** was obtained in 49% yield from the reaction of $\mathrm{Pd(PBu^t{}_3)_2}$ with $\mathrm{Ru_3(CO)_{12}}$.[4,5] Compound **1** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 1. The compound consists of a central triruthenium triangle with three Ru−Ru bonds. Each Ru−Ru bond contains a bridging $\mathrm{Pd(PBu^t{}_3)}$ grouping. Each palladium atom is bonded to two ruthenium atoms. The cluster of six metal atoms is not planar, but has a dish-like shape because each Pd atom is slightly displaced out of the $\mathrm{Ru_3}$ plane to the same side. The Ru−Ru bonds, Ru(1)−Ru(2) = 2.9191(12) Å, Ru(1)−Ru(3) = 2.9418(12) Å, Ru(2)−Ru(3) 2.9690(12) Å, are significantly longer than those in $\mathrm{Ru_3(CO)_{12}}$, 2.854(1) Å.[6] Each ruthenium atom contains four carbonyl ligands, but one of these bridges to a palladium atom. The molecule can be viewed as a tris-$\mathrm{Pd(PBu^t{}_3)}$ adduct of $\mathrm{Ru_3(CO)_{12}}$ with the $\mathrm{Pd(PBu^t{}_3)}$ groups being generated from the $\mathrm{Pd(PBu^t{}_3)_2}$ by the loss of one of its $\mathrm{PBu^t{}_3}$ donors. The palladium atom of the $\mathrm{Pd(PBu^t{}_3)}$ fragment contains only 12 electrons and will be a strong Lewis acid. If two electrons are donated to it from a Ru−Ru bond, then the electron count at the palladium atom would be increased to 14, as it was in the parent $\mathrm{Pd(PBu^t{}_3)_2}$ (see model **A**). This is conceptually similar to the well-known protonation of the metal−metal bonds of polynuclear metal complexes that occurs in strongly protic media.[3] The Pd−Ru interactions in **1** are however more complex than this simple model and include additional stabilization by bonding to a bridging carbonyl ligand. One could envisage models with even greater donation of electrons from the cluster to the palladium atom. For example, the palladium atom in the model **B** achieves a formal electron count of 16, if one counts one electron from the bridging CO ligand and two electrons via a donor:acceptor metal−metal bond from a second ruthenium atom. The best description of the bonding will probably prove to be some combination of these models and will have to be determined by more sophisticated molecular orbital calculations.

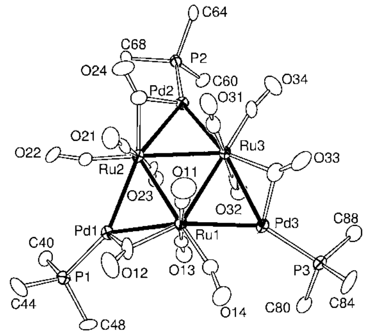


Figure 1. ORTEP diagram of $\mathrm{Ru_3(CO)_{12}[Pd(PBu^t{}_3)]_3}$ **1** showing 40% probability thermal ellipsoids. The methyl groups on the phosphine ligands have been omitted for clarity. Selected interatomic distances (Å) are: Ru(1)−Ru(2) 2.9191(12), Ru(1)−Ru(3) 2.9418(12), Ru(2)−Ru(3) 2.9690(12), Ru(1)−Pd(1) 2.7877(12), Ru(1)−Pd(3) 2.7962(12), Ru(2)−Pd(2) 2.7928(12), Ru(2)−Pd(1) 2.8398(11), Ru(3)−Pd(3) 2.8050(12), Ru(3)−Pd(2) 2.8310(12).

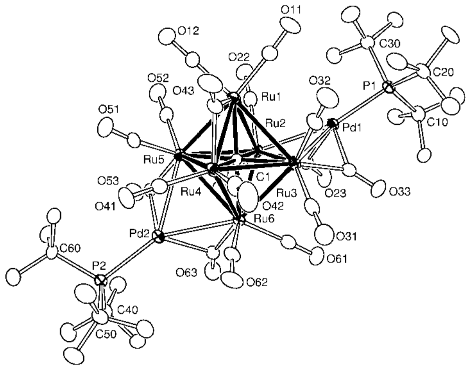
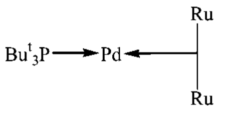
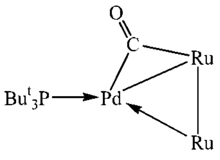


Figure 2. ORTEP diagram of $\mathrm{Ru_6(CO)_{17}(C)[Pd(PBu^t{}_3)]_2}$ **2** showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) for isomer 1 are: Pd(1)−Ru(2) 2.7790(6), Pd(1)−Ru(3) 2.8319(6), Pd(2)−Ru(6) 2.8011(6), Pd(2)−Ru(5) 2.8453(6), Ru(1)−Ru(4) 2.8429(6), Ru(1)−Ru(5) 2.8656(6), Ru(1)−Ru(3) 2.9482(6), Ru(1)−Ru(2) 3.0066(6), Ru(2)−Ru(5) 2.8590(6), Ru(2)−Ru(6) 2.8619(6), Ru(2)−Ru(3) 2.9749(6), Ru(3)−Ru(6) 2.8584(6), Ru(3)−Ru(4) 2.8643(6), Ru(4)−Ru(6) 2.9363(6), Ru(4)−Ru(5) 2.9588(6), Ru(5)−Ru(6) 2.9936(6).

We have also investigated the reaction of $\mathrm{Pd(PBu^t{}_3)_2}$ with $\mathrm{Ru_6(CO)_{17}(C)}$.[7] This reaction yielded the dipalladium complex $\mathrm{Ru_6(CO)_{17}(C)[Pd(PBu^t{}_3)]_2}$ **2** in 33% yield.[5,8] Once again there was no loss of CO from the ruthenium reagent. Compound **2** exists as two isomers in the solid state, and both isomers can be viewed as bis-$\mathrm{Pd(PBu^t{}_3)}$ adducts of $\mathrm{Ru_6(CO)_{17}(C)}$. In one isomer the $\mathrm{Pd(PBu^t{}_3)}$ groups bridge two edges of the $\mathrm{Ru_6}$ octahedron, see Figure 2. In the other isomer, Figure 3, one $\mathrm{Pd(PBu^t{}_3)}$ group bridges an edge of the $\mathrm{Ru_6}$ octahedron while the other $\mathrm{Pd(PBu^t{}_3)}$ group serves as a triple bridge. In the latter case, the three Ru−Ru bonds donate six electrons to the Pd atom, and the electron configuration at the palladium atom is increased to 18. The Ru−Ru bond distances in the $\mathrm{Ru_6}$ cluster are similar to those found in the parent compound.[9]



A



B

---

* To whom correspondence should be addressed. E-mail: adams@mail.chem.sc.edu.

10.1021/ja017486j CCC: $22.00 © 2002 American Chemical Society

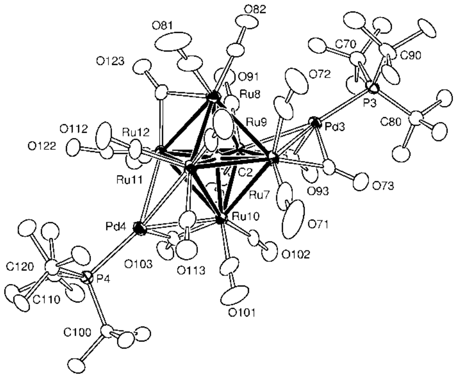


Figure 3. $Ru_6(CO)_{17}(C)[Pd(PBu^t{}_3)]_2$ isomer 2: Pd(3)−Ru(7) 2.7806(6), Pd(3)−Ru(9), 2.8423(6), Pd(4)−Ru(10) 2.8050(6), Pd(4)−Ru(12) 2.8828(6), Pd(4)−Ru(11) 3.0531(6), Ru(7)−Ru(11) 2.8587(6), Ru(7)−Ru(10) 2.8855(6), Ru(7)−Ru(8) 2.8994(6), Ru(7)−Ru(9) 2.9981(6), Ru(8)−Ru(12) 2.8289(6), Ru(8)−Ru(11) 2.8975(6), Ru(8)−Ru(9) 2.9483(6), Ru(9)−Ru(12) 2.8780(6), Ru(9)−Ru(10) 2.8928(6), Ru(10)−Ru(11) 2.9261(6), Ru(10)−Ru(12) 3.0914(6), Ru(11)−Ru(12) 2.9396(6).

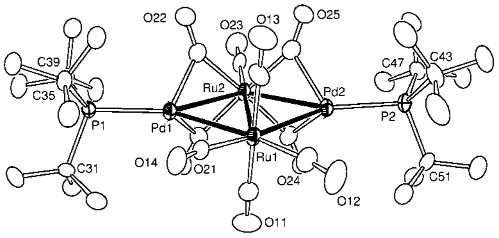


Figure 4. ORTEP diagram of $Ru_2(CO)_9[Pd(PBu^t{}_3)]_2$ **3** showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) are: Ru(1)−Ru(2) 3.0114(7), Pd(1)−Ru(2) 2.7863(7), Pd(1)−Ru(1) 2.8009(6), Pd(2)−Ru(2) 2.7694(6), Pd(2)−Ru(1) 2.8207(7), Pd(1)−P(1) 2.3971(13), Pd(2)−P(2) 2.3873(13).

Carbonyl ligands bridge from the Ru_6 cluster to the palladium atoms in both isomers.

Perhaps the most remarkable demonstration of the potential of the $Pd(PBu^t{}_3)$ group to drive new chemistry was obtained from the reaction of $Ru(CO)_5$ with $Pd(PBu^t{}_3)_2$. From this reaction the new dipalladium−diruthenium complex, $Ru_2(CO)_9[Pd(PBu^t{}_3)]_2$ **3**, was obtained in 40% yield.[5,10] Compound **3** was characterized structurally and is shown in Figure 4. This compound can be viewed as a dipalladium adduct of the elusive compound $Ru_2(CO)_9$. $Ru_2(CO)_9$ was first obtained by the photodecarbonylation of $Ru(CO)_5$ in 1977 and was reported to be a “very unstable” compound at room temperature.[11] The $Ru_2(CO)_9$ group in **3** is stabilized by the presence of two $Pd(PBu^t{}_3)$ groups both of which bridge one single Ru−Ru bond on opposite sides of the molecule, Ru−Ru = 3.0114(7) Å. Interestingly, the ruthenium atom Ru(2) contains five carbonyl ligands, four of which bridge to the neighboring palladium atoms. The four carbonyl ligands on Ru(1) are all of a terminal type.

There has been great interest in the preparation of bimetallic transition metal cluster complexes containing palladium.[12] Our new procedure should allow for the preparation of a much wider range of these types of compounds. Recently, bimetallic palladium−ruthenium clusters have been shown to be good precursors to supported bimetallic catalysts.[13] The new complexes reported here should also be useful precursors to supported bimetallic catalysts.

Acknowledgment. These studies were supported by the Division of Chemical Sciences of the Office of Basic Energy Sciences of the U.S. Department of Energy. We thank a reviewer for pointing out the structural model **B** having four-electron donation from the ruthenium cluster to the palladium atom in **1**.

Supporting Information Available: Details of the synthesis and characterizations of the products and tables of crystal data, atomic positional parameters, intramolecular bond distances and angles, and anisotropic thermal parameters for the structural analyses (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Ruff, J. K. *Inorg. Chem.* **1968**, *7*, 1499. (b) Butlitch, J. M.; Leonowicz, M. E.; Petersen, R. B.; Hughes, R. G. *Inorg. Chem.* **1979**, *18*, 1097. (c) Golden, J. T.; Petersen, T. H.; Holland, P. L.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1998**, *120*, 223.

(2) (a) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P. Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 854. (b) Davis, H. B.; Einstein, F. W. B.; Glavina, P. G.; Jones, T.; Pomeroy, R. K.; Rushman, P. *Organometallics* **1989**, *8*, 1030. (c) Shipley, J. A.; Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1991**, *10*, 3620. (d) Batchelor, R. J.; Davis, H. B.; Einstein, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.* **1990**, *112*, 2036. (e) Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K.; Shipley, J. A. *Inorg. Chem.* **1992**, *31*, 3155. (f) Einstein, F. W. B.; Jennings, M. C.; Krentz, R.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Inorg. Chem.* **1987**, *26*, 1341. (g) Fleming, M. M.; Pomeroy, R. K.; Rushman, P. *J. Organomet. Chem.* **1984**, 273, C33. (h) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Organometallics* **1985**, *4*, 250. (i) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1988**, *7*, 294. (j) Jiang, F.; Male, J. L.; Biradha, K.; Leong, W. K.; Pomeroy, R. K.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 5810. (k) Jiang, F.; Jenkins, H. A.; Birada, K.; Davis, H. B.; Pomeroy, R. K.; Zaworotko, M. J. *Organometallics* **2000**, *19*, 5049.

(3) (a) Nataro, C.; Thomas, L. M.; Angelici, R. J. *Inorg. Chem.* **1997**, *36*, 6000. (b) Kristjansdottir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983. (c) Wlaker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179. (d) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. (A)* **1970**, 2967. (e) Knight, J.; Mays, M. J. *J. Chem. Soc. (A)* **1970**, 711.

(4) $Ru_3(CO)_{12}$ (10.3 mg, 0.016 mmol) dissolved in 15 mL of CH_2Cl_2 was allowed to react with 37.0 mg of $Pd(PBu^t{}_3)_2$ (0.088 mmol) at 25 °C for 30 min. The solution was concentrated, and 10 mL of hexane was added. Upon cooling to −80 °C, 13.4 mg of crystals of blue $Ru_3(CO)_{12}[Pd(PBu^t{}_3)]_3$ **1** formed, 49% yield. Spectral data for **1**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2056 (m), 2004 (vs), 1984 (s, sh), 1948 (s), 1819 (m). ^1H NMR (in $CDCl_3$) $\delta = 1.43$ ppm (d, CH_3, $^3J_{P-H} = 12.3$ Hz). $^{31}P\{^1H\}$ NMR (in $CDCl_3$) $\delta = 81.06$ ppm. Anal. Calcd C 36.82, H 5.18. Found C 36.47, H 5.25. Crystal Data for **1**: monoclinic, space group = $P2_1/c$, $a = 24.663(2)$ Å, $b = 14.9128(13)$ Å, $c = 16.4277(14)$ Å, $\beta = 91.909(2)°$, $Z = 4$, for 4571 reflections, R1 = 0.0437, wR2 = 0.0759 for $I > 2\sigma$.

(5) Diffraction data were collected on a Bruker APEX diffractometer using Mo Kα radiation. The structure was solved by direct methods and refined on F^2 by using the SHELXTL structure solving program library

(6) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(7) Nicholls, J. N.; Vargas, M. D. *Inorg. Synth.* **1989**, *26*, 283.

(8) $Ru_6(CO)_{17}(C)$ (20 mg, 0.018 mmol) was dissolved in 25 mL of CH_2Cl_2. 29.3 mg of $Pd(PBu^t{}_3)_2$ (0.057 mmol) was added, and the solution was then stirred at 25 °C for 30 min. The product was separated by TLC on silica gel to yield 10.3 mg (33%) of $Ru_6(CO)_{17}(C)[Pd(PBu^t{}_3)]_2(\mu_6\text{-}C)$ **2**. Spectral data for **2**: IR ν_{CO} (cm^{-1} in hexane): 2074 (w), 2046 (m), 2038 (vs), 2025 (m, sh), 2019 (s), 1880 (w, br), 1825 (w, br). ^1H NMR (in $CDCl_3$) $\delta = 1.46$ ppm (d, CH_3, $^3J_{P-H} = 12.6$ Hz). $^{31}P\{^1H\}$ NMR (in $CDCl_3$) $\delta = 82.28$ ppm. Anal. Calcd C 29.45, H 3.15. Found C 29.71, H 2.99. Crystal Data for **2**: orthorhombic, space group = $P2_12_12_1$, $a = 15.1983(11)$ Å, $b = 19.7491(15)$ Å, $c = 35.841(3)$ Å, $Z = 8$, for 20374 reflections, R1 = 0.0296, wR2 = 0.0559 for $I > 2\sigma$.

(9) Braga, D.; Grepioni, F.; Dyson, P. J.; Johnson, B. F. G.; Frediani, P.; Bianchi, M.; Piacenti, F. *J. Chem. Soc., Dalton Trans.* **1992**, 2565.

(10) $Ru_3(CO)_{12}$ (11.1 mg, 0.017 mmol) was converted into $Ru(CO)_5$ by irradiating (UV) under a CO atmosphere. 14.0 mg of $Pd(PBu^t{}_3)_2$ (0.027 mmol) was added to the solution at 0 °C, and the solution was then stirred for 3 h, with slow warming to room temperature. The product was separated on a florisil column to yield 11.5 mg (40% based on Pd) of $Ru_2(CO)_9[Pd(PBu^t{}_3)]_2$, **3**. Spectral data for **3**: IR ν_{CO} (cm^{-1} in hexane): 2020 (s), 1997 (vs), 1957 (m), 1931 (m, br), 1870 (w, br), ^1H NMR (in $CDCl_3$): $\delta = 1.48$ ppm (d, CH_3, $^3J_{P-H} = 12.5$ Hz). $^{31}P\{^1H\}$ NMR (in $CDCl_3$): $\delta = 81.03$ ppm. Anal. Calc. C 36.98, H 5.04. Found C 36.71, H 5.12. Crystal Data for **3**: monoclinic, space group = $P2_1/n$, $a = 8.6504(10)$ Å, $b = 14.4307(17)$ Å, $c = 32.545(4)$ Å, $\beta = 95.003(3)°$, $Z = 4$, for 5823 reflections, R1= 0.0439, wR2 = 0.0815 for $I > 2\sigma$.

(11) Moss, J. R.; Graham, W. A. G. *J. Chem. Soc., Dalton Trans.* **1977**, 95.

(12) (a) Lee, S.-M.; Wong W.-T. *J. Cluster Sci.* **1998**, *9*, 417. (b) Nakajima, T.; Ishiguro, A.; Wakatsuki, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 1131. (c) Brivio, E.; Ceriotti, A.; Pergola, R. D.; Garlaschelli, L.; Demartin, F.; Manassero, M.; Sansoni, M.; Zanello, P.; Laschi, F.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1994**, 3237. (d) Kuwata, S.; Mizobe, Y.; Hidai, M. *J. Am. Chem. Soc.* **1993**, *115*, 8499.

(13) (a) Hermans, S.; Raja, R.; Thomas, J. M.; Johnson B. F. G.; Sankar, G.; Gleeson, D *Angew. Chem., Int. Ed.* **2001**, *40*, 1211. (b) Raja, R.; Sankar, G.; Hermans, S.; Shephard, D. S.; Bromley, S.; Thomas, J. M.; Johnson B. F. G. *Chem. Commun.* **1999**, 1571.

JA017486J