atoms in tetramesityldisilene are moderately anti-pyramidalized.[15] It seems that the planarity of disilene frameworks is sensitive to substitution.

Acknowledgment. We are grateful to Prof. Sakurai for helpful discussions and to Prof. West for making ref 15 available prior to publication. All calculations were carried out at the Computer Center of the Institute for Molecular Science, using an IMS version of the GAUSSIAN80 series of programs.[16]

Registry No. 3, 90968-70-0; 4, 90968-71-1; 5, 88867-25-8; 6, 88867-24-7.

Supplementary Material Available: A listing of the optimized geometries in Figures 1 and 2 (3 pages). Ordering information is given on any current masthead page.

---

(15) (a) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; Michl, J.; West, R., submitted for publication (private communication by Prof. West). (b) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; Michl, J.; West, R. *J. Chem. Soc., Chem. Commun.* **1983**, 1010.

(16) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *10*, 406.

Synthesis, Characterization, and Reactivity of $HRu_3(CO)_{10}(CH)$ and $H_2Ru_3(CO)_9(CCO)$

Jennifer S. Holmgren and John R. Shapley*

Department of Chemistry, University of Illinois
Urbana, Illinois 61801

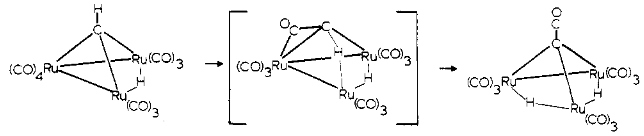
Received May 4, 1984

Summary: Treatment of $HRu_3(CO)_{10}(COMe)$ with $LiHBEt_3$ at −78 °C forms a formyl species, which above −60 °C decomposes into a mixture of $[H_2Ru_3(CO)_9(COMe)^-]$ and $[HRu_3(CO)_{10}(CHOMe)^-]$. Low-temperature extraction of this mixture provides $HRu_3(CO)_{10}(CH)$, which rearranges readily ($t_{1/2}$ = 9 min at −12 °C) into $H_2Ru_3(CO)_9(CCO)$. The latter complex appears analogous to $H_2Os_3(CO)_9(CCO)$.

Recent results have focused attention on the connection between methylidyne (≡CH) and carbonylmethylidyne (≡CCO) ligands. Thus, $HOs_3(CO)_{10}(CH)$[1] rearranges thermally into $H_2Os_3(CO)_9(CCO)$[2] and $[Fe_3(CO)_9(CCO)^{2-}]$ gives $[Fe_3(CO)_{10}(CH)^-]$ upon protonation.[3] $HOs_3(CO)_{10}(CH)$[1] was prepared by a hydride addition/protonation sequence from $HOs_3(CO)_{10}(COMe)$. We wish to describe aspects of analogous work with $HRu_3(CO)_{10}(COMe)$, which results in the synthesis of $HRu_3(CO)_{10}(CH)$ and allows observation of its facile transformation into $H_2Ru_3(CO)_9(CCO)$.

Treatment of $HRu_3(CO)_{10}(COMe)$ with $LiHBEt_3$ or $KHB(O\text{-}i\text{-}Pr)_3$ in THF at −78 °C appears to form the formyl complex $[HRu_3(CO)_9(COMe)(CHO)^-]$ (^1H NMR δ −12.2 (1 H), 14.1 (1 H)). This species is stable indefinitely below −60 °C (no change after 20 h at −65 °C), but above −60 °C both decarbonylation to give $[H_2Ru_3(CO)_9(COMe)^-]$ (δ −17.2 (s, 2 H)) and hydride transfer to give $[HRu_3(CO)_{10}(CHOMe)^-]$ (δ −12.5 (1 H), 8.4 (1 H)) occur concomitantly. The yield of $[HRu_3(CO)_{10}(CHOMe)^-]$ is maximized (55% by NMR) by maintaining the mixture at <−40 °C for an extended period (up to 160 h). Evaporating the THF and adding dry ether to the dark red residue (maintaining a low temperature) provides an orange solution and an immiscible red oil. The latter is mostly $[H_2Ru_3(CO)_9(COMe)^-]$ together with $[HRu_3(CO)_{10}(CHOMe)^-]$, and addition of $HBF_4 \cdot Et_2O$ gives an inseparable mixture of $HRu_3(CO)_{10}(CH)$ and $H_3Ru_3(CO)_9(COMe)$.[4] However, evaporation of the orange ether solution (−30 °C) provides essentially pure $HRu_3(CO)_{10}(CH)$ as an orange-yellow solid, which has been characterized spectroscopically.[5]

Scheme I



The methylidyne proton NMR resonance for $HRu_3(CO)_{10}(CH)$ occurs at δ 12.64, which is upfield of that for $HOs_3(CO)_{10}(CH)$ (δ 14.16)[1] but comparable with that for $[Fe_3(CO)_{10}(CH)^-]$ (δ 12.24).[3] The infrared spectrum of $HRu_3(CO)_{10}(CH)$ shows a band at 1902 cm^{-1}, which indicates the presence of a weakly bridging carbonyl and points to an essentially symmetric, triply bridging position for the methylidyne ligand. Such a symmetric, triply bridging structure has been postulated for $HFe_3(CO)_{10}(CCH_3)$[6] and established for $HRu_3(CO)_8(1,3\text{-}C_6H_8)(COMe)$;[7] the infrared spectrum in each case also exhibits a low-frequency band near 1900 cm^{-1}. The methylidyne ligand in $HOs_3(CO)_{10}(CH)$ is "semi" triply bridging, and the compound reacts readily at −60 °C with 1 equiv of 4-methylpyridine to yield $HOs_3(CO)_{10}(CHNC_5H_4CH_3)$.[1] In contrast, $HRu_3(CO)_{10}(CH)$ does not react with even large excesses of 4-methylpyridine or similar nucleophiles.

Near 0 °C $HRu_3(CO)_{10}(CH)$ rearranges rapidly to $H_2Ru_3(CO)_9(CCO)$.[8] The half-life at −12 °C is 9 min, $k = 1.3 \times 10^{-3}$ s^{-1} or $\Delta G^{\ddagger}_{261}$ = 19.5 kcal/mol. The analogous $HOs_3(CO)_{10}(CH)$ to $H_2Os_3(CO)_9(CCO)$ rearrangement has $\Delta G^{\ddagger}_{333}$ = 26 kcal/mol.[9] Scheme I illustrates an intermediate for the transformation [Ru–CO; ≡CH] → [Ru–H; ≡CCO], in which both migrating ligands (H and CO) are bridged between carbon and ruthenium. An analogous pathway can be proposed for the osmium system, which in addition would explain why neither $HOs_3(CO)_{10}(CSiMe_3)$[10a] nor $HOs_3(CO)_{10}(CPh)$[10b] shows any tendency to couple intramolecularly with a CO ligand. Furthermore, a closely similar intermediate could be the first species formed in the protonation of $[Fe_3(CO)_9(CCO)^{2-}]$[3b] (pro-

---

(1) Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. *J. Am. Chem. Soc.* **1983**, *105*, 140.

(2) (a) Shapley, J. R.; Strickland, D. S.; St. George, G. M.; Churchill, M. R.; Bueno, C. *Organometallics* **1983**, *2*, 185. (b) Sievert, A. C.; Strickland, D. S.; Shapley, J. R.; Steinmetz, G. R.; Geoffroy, G. L. *Ibid.* **1982**, *1*, 214. (c) Arce, A. J.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 364.

(3) (a) Kolis, J. W.; Holt, E. M.; Drezdzon, M.; Whitmire, K. A.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 6134. (b) Kolis, J. W.; Holt, E. M.; Shriver, D. F. *Ibid.* **1983**, *105*, 7307.

(4) Keister, J. B.; Horling, T. L. *Inorg. Chem.* **1980**, *19*, 2304.

(5) $HRu_3(CO)_{10}(CH)$: ^1H NMR (360 MHz, $CDCl_3$, −30 °C) δ −15.89 (s, 1 H), 12.64 (s, 1 H); IR (−20 °C, C_5H_{12}) ν_{CO} 2085 (sh), 2066 (s), 2054 (m), 2031 (vs), 2018 (s), 2004 (m), 1902 (m) cm^{-1}.

(6) Vites, J.; Fehlner, T. P. *Organometallics* **1984**, *3*, 491.

(7) Churchill, M. R.; Beanan, L. R.; Wasserman, H. J.; Bueno, C.; Rahman, Z. A.; Keister, J. B. *Organometallics* **1983**, *2*, 1179. Note that this structure shows *two* semibridging carbonyls emanating from the ML_4 center in contrast to the *one* such carbonyl proposed for $HFe_3(CO)_{10}(CCH_3)$.[6]

(8) $H_2Ru_3(CO)_9(CCO)$: FI mass spectrum (^{102}Ru), m/z 600 (M^+); IR (C_6H_{12}) ν_{CO} 2120 (m), 2084 (s), 2056 (vs), 2038 (w), 2030 (vw), 2010 (m), 2000 (w), 1965 (vw) cm^{-1}; ^1H NMR ($CDCl_3$) δ −18.08 (s). Anal. Calcd for $Ru_3C_{11}H_2O_{10}$: C, 22.11; H, 0.33. Found: C, 22.32; H, 0.50.

(9) Cree-Uchiyama, M. E.; Shapley, J. R., unpublished results.

(10) (a) Sievert, A. C.; Shapley, J. R., unpublished results. (b) Yeh, Wen-Yann; Shapley, J. R., unpublished results.

0276-7333/84/2303-1322$01.50/0

tonation of one Fe–C bond causes the CO moiety to move to more fully bridging the adjacent Fe–C bond), after which operation of the migrations in reverse gives $[Fe_3(CO)_{10}(CH)^-]$.[11]

The $H_2Ru_3(CO)_9(CCO)$ proton NMR resonance remains a sharp singlet down to −80 °C, indicating a symmetric structure. The infrared spectrum is closely similar to that of $H_2Os_3(CO)_9(CCO)$ and contains no low-frequency bands to indicate bridging carbonyls. Thus, $H_2Ru_3(CO)_9(CCO)$ is very likely isostructural with its osmium analogue.[2a] It also reacts analogously.[2b] Addition of $HBF_4 \cdot Et_2O$ to a dichloromethane solution of $H_2Ru_3(CO)_9(CCO)$ forms a white precipitate, presumably $[H_3Ru_3(CO)_9(CCO)^+]$, which dissolves upon addition of MeOH or H_2O. Subsequent workup provides $H_3Ru_3(CO)_9(CCO_2CH_3)$[4] or $H_3Ru_3(CO)_9(CCO_2H)$,[12] respectively.

Further studies with these and related organotriruthenium compounds are in progress.

Acknowledgment. This work was supported by National Science Foundation Grant CHE81-00140. Instruments supported by Grants NSF CHE79-16100 and NIH GM-27029 were utilized for NMR and mass spectra, respectively.

Registry No. $[H_2Ru_3(CO)_9(COMe)^-]$, 90990-74-2; $[HRu_3(CO)_{10}(CHOMe)^-]$, 91002-38-9; $HRu_3(CO)_{10}(CH)$, 90990-75-3; $H_3Ru_3(CO)_9(COMe)$, 71562-47-5; $H_2Ru_3(CO)_9(CCO)$, 90990-76-4; $[H_3Ru_3(CO)_9(CCO)^+]BF_4^-$, 90990-78-6; $H_3Ru_3(CO)_9(CCO_2CH_3)$, 73746-98-2; $H_3Ru_3(CO)_9(CCO_2H)$, 90990-79-7; $HRu_3(CO)_{10}(COMe)$, 71737-42-3.

---

[11] Protonation of $[Fe_3(CO)_9(CCO)^{2-}]$ with a strong acid (CF_3SO_3H) was claimed to give $HFe_3(CO)_{10}(CH)$ (δ −20.52, 12.16).[3] No evidence for rearrangement to $H_2Fe_3(CO)_9(CCO)$ was noted.

[12] $H_3Ru_3(CO)_9(CCO_2H)$: FI mass spectrum (^{102}Ru), m/z 618 (M^+); IR (C_6H_{12}) ν_{CO} 2090 (s), 2040 (s), 2031 (m, sh), 1685 (w) cm^{-1}; ^1H NMR ($CDCl_3$, −40 °C) δ −17.81 (s, 3 H), 9.44 (s, 1 H). Anal. Calcd for $Ru_3C_{11}H_4O_{11}$: C, 21.46; H, 0.65. Found: C, 21.39; H, 0.66.

Book Reviews

Comprehensive Organometallic Chemistry. The Synthesis, Reactions, and Structures of Organometallic Compounds. Vol. 6. Edited by G. Wilkinson, F. G. A. Stone, and E. W. Abel. Pergamon Press, Oxford. 1982. 1114 pages. $260.

The first quarter of Volume 6 (Chapter 37 by P. W. Jolly) is essentially a descriptive treatment of the synthesis, structure, and reactions of organonickel complexes. Since 1974, when Jolly and Wilke published "The Organic Chemistry of Nickel", the growth in this area, in the author's words, "has been more in girth than in stature". As a result, the format of Chapter 37 is largely the same as the format in "The Organic Chemistry of Nickel"; Chapters 37.2 and 37.3 on nickel tetracarbonyl and Lewis base substituted nickel carbonyl complexes, respectively, are followed by chapters on nickel hydride, alkyl, aryl, η^3-allyl, cyclobutadiene, cyclopentadienyl, and arene complexes. The vast majority of references are from later than 1973, making Chapter 37 an indispensable, exhaustive addendum to "The Organic Chemistry of Nickel". Chapters covering the use of organonickel compounds as stoichiometric reagents in organic synthesis or as catalysts are found in Chapter 56 of Volume 8 in this series.

Chapter 38 concerns the organometallic chemistry of palladium. Its nine parts are all written by P. M. Maitlis, P. Espinet, and M. J. H. Russell. In the Introduction (38.1) the authors do not state to what extent this review overlaps Maitlis' "The Organic Chemistry of Palladium" published in 1971, but it seems clear that the overlap between this article and the book is more extensive than it is in the case of nickel above. The format is largely the same as it is in "The Organic Chemistry of Palladium" with sections on complexes of palladium(0), palladium(I), and cluster complexes, compounds with palladium–carbon σ bonds, monoolefin and acetylene complexes of palladium, diene complexes of palladium, allylic complexes of palladium(II), cyclopentadienyl and arene complexes of palladium(II), and palladium complexes derived from reactions with acetylenes. The use of organopalladium compounds in organic synthesis and catalysis is covered in Chapter 57 of Volume 8; the overlap between Chapter 57 and Chapter 38 is minimal.

Chapter 39, "Platinum", is written by F. R. Hartley. In contrast to Chapters 37 and 38, all the (~1700) references in Chapter 39 are gathered at the end of the chapter. One advantage is that duplication of references in different sections is thereby avoided. Approximately half the references are post-1973, the year the author published "The Chemistry of Palladium and Platinum". The 250-page chapter includes sections on carbonyl, isocyanide, carbene, ylide, alkyl, olefin, acetylene, and π-allyl complexes, as well as a section on CH bond activation, and short sections on complexes containing x-bonded rings (x = 4–8).

The next four chapters are devoted to complexes in which the transition metal is bonded to a different transition metal or a main-group metal.

Chapter 40 (by D. A. Roberts and G. L. Geoffroy) concerns compounds containing bonds between different transition metals. The chapter is organized into three sections—synthesis, characterization, and reactivity. A 50-page comprehensive list of heteronuclear metal–metal bond compounds is provided. There are 245 references. Curiously, references for the comprehensive list and tables are each listed separately from the references for the text, a practice that necessarily encourages duplication. The topic of heteronuclear transition-metal bonds is a difficult one to review at this stage, since there is relatively little detailed understanding of the formation or reactions of such species, in contrast to a wealth of structural studies. This contribution is a worthwhile effort to organize the diverse findings in this developing area.

The two chapters on compounds containing a bond between a transition metal and a group 3B element are written by K. B. Gilbert, S. K. Boocock, and S. G. Shore (41.1; Boron) and S. K. Boocock and S. G. Shore (41.2; Al, Ga, In, Tl). Chapter 41.1 emphasizes borohydride derivatives. It complements nicely parts of Chapter 5.3 in Volume 1 (Boron Ring Systems as Ligands to Metals) and Chapter 5.5 (Metallacarboranes and Metallaboranes). Much of the material in the chapter on Al, Ga, In, and Tl is brought together here for the first time. The emphasis in each chapter is on synthesis. Discussion of structural details and mechanisms is kept to a minimum.

The last two chapters deal with transition metal–M bonds where M is mercury, cadmium, zinc, or magnesium (42 by J. M. Burlitch) or silicon, germanium, tin, or lead (43 by K. M. Mackay and B. K. Nicholson). They both update earlier reviews as well as add a large amount of new material. There is some repetition as to the type of compound that has been prepared (often a metal carbonyl–M complex) but there are also many exotic animals here that pique one's curiosity. Reviews of the more well-developed areas (e.g., transition metal–Si bonds) are thorough and well organized.

All in all, Volume 6 is a valuable component of the series. As with most other volumes, this one is intended for the specialist.