complexed to a single oxygen atom, the chlorine center would distort toward (but certainly not to) a trigonal geometry; in the more likely event of protonation of two oxygens, distortion (clearly not complete) in the direction of a square-planar geometry about chlorine would be expected. Either of these two types of distortion (even if fairly small) would lower the energy of the LUMO of the perchlorate[6] group (which would be expected to have the same symmetry with respect to a Ti–O–Cl axis as the electron-donor orbital of Ti). Once interaction of an electron-donor orbital (titanium t_{2g}) and an electron-acceptor orbital (involving chlorine p and/or d π orbitals) had been facilitated by distortion, electron transfer should be rapid. On this view, distortion of perchlorate to permit electronic overlap (the third step above) is rate determining.

In proposing the alternative mechanism, Taube suggested[3] that the acid dependence reported for the Ti^{3+}–perchlorate reaction might be an artifact, since no acid dependence would be expected on the basis of his hypothesis. The previously reported acid dependence for the Ti^{3+}–perchlorate reaction is consistent with the present results. Rates of redox reactions of Ti^{3+} are normally inversely proportional to $[H^+]$, because reaction goes through $Ti(OH)^{2+}$. If distortion of a doubly protonated intermediate were also operative in the Ti^{3+}–perchlorate reaction, the net result would be a term with a first-order dependence on acid, as reported. In the case of reduction of perchlorate ion by (*N*-(hydroxyethyl)ethylenediaminetriacetato)aquotitanium(III), the amino acid ligand prevents proton dissociation from Ti^{3+} and blocks the $TiOH^{2+}$ path, with the result that the acid dependence is large. Our present results are consistent with Kallen and Earley's rationalization of the bizarre rate order of cation reduction of perchlorate. The difficulty, noted by Taube, of reconciling an acid dependence with the alternate (-yl ion) rationalization indicates that the present results are not consistent with that alternate mechanism.

Acknowledgment. $LiCF_3SO_3$ and CF_3SO_3H solution were kindly supplied by Dr. Patrizia Barone. We are grateful for helpful discussion with Professors Karl Wieghardt and Miklos Kertesz and to Ke-jean Lu for experiments on the initial irregularity.

Registry No. Ti(Hedta), 77704-13-3; ClO_4^-, 14797-73-0.

(6) Johansen, H. *Chem. Phys. Lett.* **1971**, *11*, 466.

Notes

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

Reactions at the Metal Vertex of a Ruthenacarborane Cluster. Activation of Carbon Monoxide by *closo*-3,3,3-$(CO)_3$-3,1,2-$RuC_2B_9H_{11}$

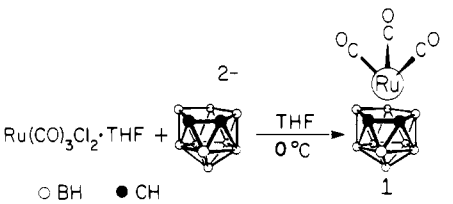
Paul E. Behnken and M. Frederick Hawthorne*

Received December 20, 1983

Activation of coordinated CO with respect to nucleophilic attack has been proposed to be an important aspect of the homogeneous catalysis of the water gas shift reaction as well as organic reductions employing CO/H_2O mixtures.[1] Furthermore, this mode of activation represents the primary route to transition-metal formyl complexes, proposed as intermediates in the conversion of CO/H_2 mixtures to oxygenated organic products.[2] In light of these observations, we have investigated the chemistry of *closo*-3,3,3-$(CO)_3$-3,1,2-$RuC_2B_9H_{11}$ (**1**), which we have found to be highly reactive toward nucleophiles. The results of this study and subsequent chemistry will provide the basis for this note.

Results and Discussion

The synthesis of **1** was first reported by Siedle[3] who reacted $[Ru(CO)_3Cl_2]_2$ with 7,8-$C_2B_9H_{11}^{2-}$ in refluxing THF to produce **1** in 7% yield. We have improved the yield to 65% by employing a slow addition of 7,8-$C_2B_9H_{11}^{2-}$ to a stirred THF solution of $Ru(CO)_3Cl_2$·THF[4] at 0 °C (eq 1). In this way, exposure of the product **1** to the nucleophilic $C_2B_9H_{11}^{2-}$ dianion is minimized and the yield is optimized. The high terminal C≡O stretching frequencies of **1** (2090, 2030 cm^{-1}) suggests



(1)

that these ligands should be reactive toward nucleophiles since reduced π^* back-bonding effectively decreases the electron density at the carbonyl carbon.[5] In fact, **1** was found to react rapidly with a range of nucleophiles, the results being summarized in Scheme I.

Addition of 1 molar equiv of $K^+B(sec\text{-}C_4H_9)_3H^-$ to an NMR tube containing a THF solution of **1** cooled to -78 °C resulted in the observation of a singlet in the ^1H FTNMR spectrum at δ 14.1, attributed to the anionic formyl complex **2** (Scheme I). Warming the NMR tube to 0 °C converts **2** to the anionic dicarbonyl hydride complex **3** with a time for half-reaction of ca. 30 min. This mode of decomposition of the formyl complex **2** is well established[2] although the stability of **2** differs markedly from that of the neutral analogue, $(C_5H_5)Ru(CO)_2CHO$, which decomposes rapidly at -90 °C.[6]

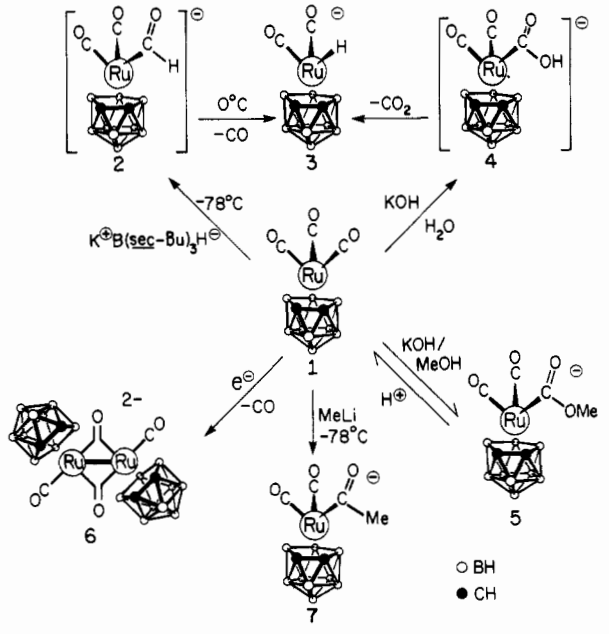
The complex **3** was also prepared by the reaction of **1** in THF with an excess of aqueous KOH (Scheme I). This reaction may be viewed as the decarboxylation of an intermediate hydroxy carbonyl adduct or metallocarboxylic acid **4**. Although this intermediate was not directly observed, reaction of **1** with methanolic KOH quantitatively produced the metallocarboxylic acid ester **5**. This complex was thermally stable but reacted rapidly with acid to regenerate **1** and methanol (Scheme I).

Compounds **3** and **5** have precedent with the analogous $(C_5H_5)Ru(CO)_2H$[7] and $(C_5H_5)Ru(CO)_2COOMe$[8] but differ

(1) Gross, D. C.; Ford, P. C. *Inorg. Chem.* **1982**, *21*, 1704 and references therein.
(2) For a recent review see: Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.
(3) Siedle, A. R. *J. Organomet. Chem.* **1975**, *90*, 249.
(4) Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1967**, 1238.
(5) Angelici, R. J.; Blacik, L. J. *Inorg. Chem.* **1972**, *11*, 1754.
(6) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsy, S. G. *J. Mol. Catal.* **1981**, *13*, 43.
(7) Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133.

0020-1669/84/1323-3420$01.50/0

Scheme I. Reactions of 1 with Nucleophiles



with respect to air sensitivity. While both the cyclopentadienyl ruthenium carbonyl hydride and metallocarboxylic acid ester are reported to be very air-sensitive, both **3** and **5** are stable in air as solids and solutions decompose in air only over a period of hours.

Complex **1** was also reduced with Na/Hg amalgam to form the binuclear dianionic complex **6** (Scheme I). This complex is spectroscopically similar to the crystallographically characterized iron analogue, $[Fe(CO)_2C_2B_9H_{11}]_2^{2-}$,[9] with the exception of exhibiting only one terminal C≡O stretch (1910 cm^{-1}). Complex **6** may therefore exist in the solid state in a centrosymmetric trans configuration, unlike the iron complex that has a *cis* configuration of the carborane ligands. Complex **6** was also observed as a major side product in the reaction of **1** with stoichiometric amounts of aqueous KOH, along with **3**. This may result from nucleophilic attack on **1** by **3** in the presence of base as **3** could be generated cleanly by slow addition of **1** to an excess of aqueous KOH, thereby minimizing the exposure of **1** and **3**.

Reaction of 1 molar equiv of MeLi with **1** in THF -78 °C afforded the anionic acyl complex **7** (Scheme I). Complex **7** was isolated as the tetramethyl- and trimethylammonium as well as the $[K(18\text{-crown-6})]^+$ salt. The dependence of the acyl C=O stretch on the counterion (1610 cm^{-1} for Me_4N^+, $[K(18\text{-crown-6})]^+$; 1570 cm^{-1} for Me_3NH^+) suggests some carbenoid character of the anionic acyl functionality. The subsequent chemistry that may be derived from this complex is currently under investigation.

The facile conversion of **1** to **3** with concomitant oxidation of CO to CO_2 suggested the possible utility of **1** as a catalyst for the water gas shift reaction (WGSR; eq 2). The WGSR

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

is commercially important as a means of altering $CO:H_2$ ratios in synthesis gas. Homogeneous catalysis of this reaction under mild conditions would thermodynamically favor formation of product as the reaction is midly exothermic.[10] For these reasons, the usefulness of **1** as a WGSR catalyst under mild conditions was evaluated.

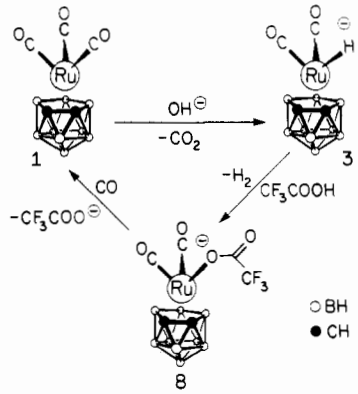


Figure 1. Stoichiometric conversion of a WGSR cycle employing **1**.

Table I. Conditions for Evaluation of 1 as a WGSR Catalyst

no.	[1], mM	P(CO), mm	solvent	T, °C	[acid/base], M	time, h
1	11.5	690	10% H_2O/*n*-PrOH	80		48
2	11.5	687	10% H_2O/*n*-PrOH	80	13.4 (HBF_4)	24
3	12.6	712	H_2O	80	38.2 (KOH)	27
4	15.8	810	50% acetone/H_2O	60		43
5	15.8	800	50% acetone/H_2O	60	18.4 (HBF_4)	24

Reaction of **3** with CF_3COOH in acetone resulted in the rapid formation of a new complex **8** (Figure 1). Conversion of **3** to **8** was accompanied by the conversion of 1.0 equiv of acetone to 2-propanol (confirmed by VPC analysis of the reaction solvent). Complex **3** could also be converted to **8** by reaction with CF_3COOH in THF (reflux, 6 h) presumably via loss of H_2. Conversion of **8** to **1** could be accomplished by stirring THF solutions of **8** under CO (1 atm) at room temperature for 1 day (Figure 1). The facility of this reaction may be due to the trifluoroacetate anion serving as a good leaving group from an anionic complex. Furthermore, the reaction is promoted by strong acid (CF_3COOH), suggesting that complex **8** can be protonated, thus labilizing the trifluoroacetate ligand.

The ability of **1** to serve as a WGSR catalyst under mild conditions was evaluated under acidic, neutral, and basic conditions (Table I). Gas chromatographic analysis of the gas over the reactions at the times indicated revealed only small amounts of CO_2 (<1 equiv/Ru) in experiments 3 and 5. The composition of the solutions was monitored by ^{11}B FTNMR spectroscopy and revealed **1** to be the dominant species in experiments 1, 2, 4, and 5. Cooling these solutions and dilution with H_2O resulted in quantitative recovery of **1**. The major species in experiment 3 were **3** and **6**, which were converted to **1** by injection of 50 μL of concentrated HBF_4, resulting in the quantitative precipitation of **1** from the aqueous solution. Conversion of **6** to **1** under acidic conditions presumably involves H_2 evolution from the binuclear center subsequent to protonation. These experiments, despite the inactivity of **1** as a WGSR catalyst, confirmed the hydrolytic stability of these intermediates. Experiments 4 and 5 were performed to evaluate the possibility that **1** might serve as a catalyst for the reduction of acetone to 2-propanol with CO/H_2O mixtures, as **3** was shown to be effective in the stoichiometric reduction of acetone under acidic conditions.

The ^{11}B FTNMR analyses and quenching studies of the reaction solutions suggest the inactivity of **1** as a WGSR catalyst is a consequence of the conflicting pH demands of individual steps in the proposed mechanism. The alkaline conditions necessary for attack on **1** and decarboxylation to produce **3** are prohibitive for the conversion of **3** back to **1**, which requires acidic conditions. Similar explanations have been used to explain the low activity of $Fe(CO)_5$ as a WGSR catalyst under mild conditions.[11]

(8) Kruse, A. E.; Angelici, R. J. *J. Organomet. Chem.* **1970**, *24*, 231.
(9) (a) Hawthorne, M. F.; Ruhle, H. W. *Inorg. Chem.* **1969**, *8*, 176. (b) Greene, P. T.; Bryan, R. F. *Inorg. Chem.* **1970**, *11*, 1464.
(10) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31.

Experimental Section

All reactions, except where noted, were carried out under an argon atmosphere employing Schlenk techniques. Me_3NH^+-7,8-$C_2B_9H_{11}^-$[12] and $[Ru(CO)_3Cl_2]_2$[13] were prepared by literature methods. Heptane and THF were distilled under dinitrogen from potassium metal. Diethyl ether was distilled from sodium/potassium alloy and toluene distilled from sodium metal under dinitrogen. KOH (Mallinckrodt), $K^+B(sec\text{-}C_4H_9)_3H^-$ (Aldrich), and CH_3Li (Alfa) were purchased and used as supplied.

NMR data are listed in ppm and referenced to internal isotopic impurities in the NMR solvent and to external BF_3·EtOEt for ^{11}B spectra. ^{11}B FTNMR data were collected at 126.7 MHz, employing an instrument designed and built by Prof. F. A. L. Anet of this department. ^1H FTNMR data were obtained at 200.133 MHz on a Bruker WP-200 spectrometer. IR data were measured with a Perkin-Elmer 137 spectrometer. Microanalyses were performed by Schwarzkopf Laboratories, Woodside, NY, and Galbraith Laboratories, Knoxville, TN.

Preparation of *closo*-3,3,3-$(CO)_3$-3,1,2-$RuC_2B_9H_{11}$ (1). Me_3NH^+-7,8-$C_2B_9H_{12}^-$ (1.51 g, 7.8 mmol) was reacted with 3.0 g of NaH (75 mmol) in 75 mL of THF to generate the 7,8-$C_2B_9H_{11}^{2-}$ dianion in situ according to a published procedure.[14] The reaction was filtered and added dropwise to a stirred solution of 2.20 g of $[Ru(CO)_3Cl_2]_2$ (8.6 mmol of Ru) in 80 mL of THF maintained at 0 °C. After the addition was complete, the reaction was warmed to room temperature and added to a mixture of 100 mL of H_2O and 100 mL of toluene. The organic layer was separated and washed three times with 50-mL portions of H_2O, dried with $MgSO_4$, and reduced to dryness under vacuum, yielding an orange residue. The residue was dissolved in 50 mL of dry toluene, treated with silica gel, and filtered. The silica gel was washed thoroughly with dry toluene (4 × 50 mL), and the filtrates were combined and reduced to a small volume. The product was crystallized by addition of heptane and vacuum dried to yield 1.62 g of **1** (65%) as a buff-colored crystalline solid.

^{11}B NMR (acetone) δ −17.8 (d, 3 B, J_{B-H} = 164 Hz), −8.9 (d, 2 B, J_{B-H} = 151 Hz), −5.0 (d, 2 B, J_{B-H} = 150 Hz), −3.7 (d, 1 B, J_{B-H} = 151 Hz), +8.7 (d, 1 B, J_{B-H} = 145 Hz); IR (Nujol) 2510 (B–H), 2090, 2030 cm^{-1} (MC≡O).

Preparation of [K(18-crown-6)]$^+$[*closo*-3,3-$(CO)_2$-3-(H)-3,1,2-$RuC_2B_9H_{11}$]$^-$ (3). (a) A solution of **1** (0.50 g, 1.57 mmol) and 0.45 g of 18-crown-6 (1.7 mmol) in THF (50 mL) was added dropwise to a solution of 0.88 g of KOH (16 mmol) in 50 mL of H_2O at 0 °C. The reaction was warmed to room temperature and reduced to small volume, producing a white solid. The solid was dried and crystallized from THF by addition of heptane, yielding 0.80 g of **3** as colorless crystals (86%).

(b) A solution of **1** (0.25 g, 0.79 mmol) in 25 mL of THF was cooled to −78 °C and 0.79 mL of $K^+B(sec\text{-}C_4H_9)_3H^-$ (1.0 M in THF, 0.79 mmol) added dropwise with stirring. The reaction was stirred at −78 °C for 30 min and warmed to 0 °C for 2 h followed by addition of 0.22 g of 18-crown-6 (0.86 mmol). The solution was reduced to small volume and product crystallized by addition of 40 mL of ether. The off-white crystals were collected by filtration and washed thoroughly with ether to yield 0.35 g of **3** (75%).

^{11}B NMR (acetone) δ −22.0 (d, 3 b, J_{B-H} = 148 Hz), −12.6 (d, 2 B, J_{B-H} = 140 Hz), −9.5 (d, 2 B, J_{B-H} = 137 Hz), −6.8 (d, 1 B, J_{B-H} = 129 Hz), −4.9 (d, 1 B, J_{B-H} = 142 Hz); ^1H NMR ($CDCl_3$) δ 3.64 (s, 24 H, $-CH_2-$), 2.88 (br s, 2 H, carborane C–H), −8.40 (s, 1 H, Ru–H); IR (Nujol)2500 (B–H), 1990, 11925 (MC≡O), 1105 cm^{-1} (C–O). Anal. Calcd for $C_{16}H_{34}B_9K_1O_8Ru$: C, 32.47; H, 5.79; B, 16.44; K, 6.60; Ru, 17.08. Found: C, 32.37; H, 5.90; B, 16.27; K, 6.81; Ru, 16.74.

Preparation of [K(18-crown-6)]$^+$[*closo*-3,3-$(CO)_2$-3-(CO_2Me)-3,1,2-$RuC_2B_9H_{11}$]$^-$ (5). A solution of 0.500 g of **1** (1.57 mmol) in 25 mL THF was stirred during the dropwise addition of 8.5 mL of 0.186 N KOH/MeOH (1.57 mmol). The reaction was stirred 1 h followed by the addition of 0.44 g of 18-crown-6 (1.7 mmol). The solvent was removed and the white precipitate crystallized twice from CH_2Cl_2 by addition of heptane and diethyl ether, respectively, to yield 0.90 g of **5** as white microcrystals (88%).

^{11}B NMR (acetone) δ −22.0 (d, 2 B, J_{B-H} = 156 Hz), −20.4 (d, 1 B, J_{B-H} = 212 Hz), −11.3 (d, 2 B, J_{B-H} = 142 Hz), −9.0 (d, 1 B, J_{B-H} = 137 Hz), −3.8 (d, 1 B, J_{B-H} = 134 Hz); ^1H NMR (acetone-d_6) δ 3.66 (s, 24 H, $-CH_2-$), 3.48 (s, 3 H, $-CO_2CH_3$), 2.85 (br s, 2 H, carborane C–H); IR (Nujol) 2500 (B–H), 2010, 1950 (MC≡O), 1610 (C═O), 1105 cm^{-1} (C–O). Anal. Calcd for $C_{18}H_{38}B_9KO_{10}Ru$: C, 33.16; H, 5.87; B, 14.92; K, 6.00; Ru, 15.50. Found: C, 33.37; H, 5.92; B, 14.35; K, 6.09; Ru, 15.49.

Preparation of [K(18-crown-6)]$^+_2$[*closo*-3-CO-3,3′-(μ-CO)-3,12-$RuC_2B_9H_{11}$]$_2^{2-}$ (6). A THF (25 mL) solution of **1** (0.262 g, 0.83 mmol) was cannulated over a 5% Na/Hg amalgam at 0 °C, resulting in an immediate color change to orange. The reaction was cannula filtered into 25 mL of 95% EtOH containing 65 mg of KCl and 230 mg of 18-crown-6 (0.87 mmol) and reduced to small volume, yielding an orange solid. The precipitate was dissolved in a minimum of acetone and filtered, and product was crystallized by addition of 95% EtOH. The orange plates were collected by filtration, washed with 95% EtOH, and vacuum dried (0.264 g, 54%).

^{11}B NMR (acetone) δ −21.0 (d, 3 B, J_{B-H} = 148 Hz), −10.8 (d, 2 B, J_{B-H} = 139 Hz), −8.8 (d, 3 B, J_{B-H} = 129 Hz), −0.8 (d, 1 B, J_{B-H} = 132 Hz); ^1H NMR (acetone-d_6) δ 3.66 (s, 24 H, $-CH_2-$), 2.26 (br s, 2 H, carborane C–H); IR (Nujol) 2500 (B–H), 1910 cm^{-1} (MC≡O), 1735 (C═O), 1105 cm^{-1} (C–O). Anal. Calcd for $C_{32}H_{70}B_{18}K_2O_{16}Ru_2$: C, 32.41; H, 5.95; B, 16.41; K, 6.59; Ru, 17.05. Found: C, 32.81; H, 6.03; B, 17.85; K, 6.84; Ru, 17.25.

Preparation of [Me_4N]$^+$[*closo*-3,3-$(CO)_2$-3-$(COCH_3)$-3,1,2-$RuC_2B_9H_{11}$]$^-$ (7). A solution of 0.30 g of **1** (0.95 mmol) in 30 mL of THF was cooled to −78 °C, and 0.72 mL of CH_3Li/Et_2O (1.3 M, 0.94 mmol) was added slowly. The reaction was warmed slowly to room temperature and cannulated into 10 mL of H_2O containing 0.10 g of $Me_4N^+Cl^-$ (1.1 mmol). The solution was reduced in volume and resultant white precipitate collected, dried, and crystallized from THF by addition of heptane to yield 0.273 g of **7** (0.67 mmol, 71%).

^{11}B NMR (acetone) δ −21.3 (d, 3 B, J_{B-H} = 148 Hz), −11.6 (d, 2 B, J_{B-H} = 140 Hz), −7.9 (d, 3 B, J_{B-H} = 137 Hz), −4.8 (d, 1 B, J_{B-H} = 145 Hz); ^1H NMR (acetone-d_6) δ 3.44(s, 12 H, $(CH_3)_4N$), 2.63 (br s, 2 H, carborane C–H), 2.53 (s, 3 H, $RuC(O)CH_3$); IR (Nujol) 2500 (B–H), 2010, 1940 (MC≡O), 1610 cm^{-1} (C═O). Anal. Calcd for $C_{10}H_{26}B_9NO_3Ru$: C, 29.53; H, 6.44; B, 23.93; N, 3.44; Ru, 24.86. Found: C, 29.71; H, 6.29; B, 24.59; N, 3.20; Ru, 25.05.

Preparation of [K(18-crown-6)]$^+$[*closo*-3,3-$(CO)_2$-3-$(OCOCF_3)$-3,1,2-$RuC_2B_9H_{11}$]$^-$ (8). A solution of 0.26 g of **3** (0.44 mmol) in acetone was reacted with 300 μL of CF_3COOH (3.9 mmol) at room temperature, accompanied by a color change to orange. The reaction was reduced in volume and product crystallized by addition of ether. The orange microcrystals were collected by filtration, washed with ether, and vacuum dried (0.21 g, 68%).

^{11}B NMR (acetone) δ −21.5 (d, 2 B, J_{B-H} = 155 Hz), −17.6 (d, 1 B, J_{B-H} = 172 Hz), −10.1 (d, 1 B, J_{B-H} = 151 Hz), −7.8 (d, 4 B, J_{B-H} = 143 Hz), +1.4 (d, 1 B, J_{B-H} = 135 Hz); ^1H NMR (CD_2Cl_2) δ 3.65 (s, 24 H, $-CH_2-$), 3.18 (br s, 2 H, carborane C–H); IR (Nujol) 2500 (B–H), 2030, 1970 (MC≡O), 1680 (C═O), 1105 cm^{-1} (C–O). Anal. Calcd for $C_{18}H_{35}B_9F_3KO_{10}Ru$: C, 30.63; H, 5.00; B, 13.78; F, 8.07; K, 5.54; Ru, 14.32. Found: C, 31.60; H, 5.15; B, 14.91; F, 8.04; K, 5.36; Ru, 14.09.

In Situ Reaction of 1 with $K^+B(sec\text{-}C_4H_9)_3H^-$. A 5-mm NMR tube equipped with a septum cap was charged with 25 mg of **1** (7.9×10^{-2} mmol) and 0.5 mL of THF-d_8, flushed with Ar and cooled to −78 °C. $K^+B(sec\text{-}C_4H_9)_3H^-$ (80 μL, 1.0 M; in THF; 8.0×10^{-2} mmol) was transferred to the NMR tube via syringe and mixing ensured by bubbling Ar through the solution. The tube was quickly transferred to the NMR probe that was cooled to 200 K. Spectra were recorded at 200 and 250 K, revealing a sharp resonance at δ 14.1, characteristic of a transition-metal formyl complex.[2] Warming the sample to 273 K resulted in the slow disappearance of this resonance with the concomitant appearance of a singlet at −8.22 ppm attributed to the characterized hydrido complex **3**. The time for the half-reaction of the formyl complex was ca. 30 min at 273 K.

Screening Procedure for 1 as a WGSR Catalyst. The apparatus consisted of a high-vacuum manifold equipped with manometer attached to a reaction flask via condenser. The reaction flask was magnetically stirred, immersed in a thermostated oil bath, and

(11) Pearson, R. G.; Mauermann, H. *J. Am. Chem. Soc.* **1982**, *104*, 500.
(12) Hawthorne, M. F.; Young, D. C.; Garrett, P. M.; Owen, D. A.; Schwerin, S. G.; Tebbe, F. N.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 862.
(13) Cotton, R.; Farthing, R. H. *Aust. J. Chem.* **1971**, *24*, 903.
(14) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.

equipped with a side arm with a septum through which gas and solution samples could be withdrawn for analysis. Typically, **1** was introduced as a solid, the flask was flushed with Ar, and solvent(s) and acid/base were transferred via syringe followed by three freeze/pump/thaw cycles. Carbon monoxide (6% methane as GC standard) was introduced and the reaction brought to temperature. Gas analyses were performed with 3 M × 4 mm column packed with Porapak Q with He carrier gas employing a thermal conductivity detector. Results are summarized in Table I.

Acknowledgment. The authors thank the Basic Science Division of the Department of Energy for generous support of this research under Grant DE-ATO3-80ER10673. We also thank the National Science Foundation for the purchase of the Bruker WP-200 FTNMR spectrometer under Grant CHE 77-05926.

Registry No. **1**, 56465-06-6; **2**, 91549-31-4; **3**, 91585-88-5; **5**, 91606-01-8; **6**, 91585-89-6; $[Me_4N][7]$, 91549-35-8; $[Me_3NH][7]$, 91549-37-0; [K(18-crown-6)][7], 91585-86-3; **8**, 91585-87-4; $[Me_3NH][7,8\text{-}C_2B_9H_{12}]$, 57409-10-6; $[Ru(CO)_3Cl_2]_2$, 22594-69-0; CO, 630-08-0.

Contribution from the Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, U.K.

Spectroelectrochemical Studies on Tris(bipyridyl)iridium Complexes: Ultraviolet, Visible, and Near-Infrared Spectra of the Series $[Ir(bpy)_3]^{3+/2+/+/0}$

Vyvyan T. Coombe, Graham A. Heath,* Alan J. MacKenzie, and Lesley J. Yellowlees*

Received July 15, 1983

Recently[1] we described the progression in absorption spectra for tris(bipyridyl)ruthenium(II), $[Ru(bpy)_3]^{2+}$ (I^{2+}) and its reduced analogues, $[Ru(bpy)_3]^{+}$ (I^{+}), $[Ru(bpy)_3]^{0}$ (I^{0}), and $[Ru(bpy)_3]^{-}$ (I^{-}). In each case we were able to assign all the observed bands in terms of characteristic electronic transitions involving noninteracting bpy^0 and bpy^- ligands (for I^+ and I^0) or discrete bpy^- ligands alone (I^-). We thus concluded that the complexes should be formulated with localized charge distributions, namely $[Ru^{II}(bpy^0)_3]^{2+}$, $[Ru^{II}(bpy^0)_2(bpy^-)]^{+}$, $[Ru^{II}(bpy^0)(bpy^-)_2]^{0}$, and $[Ru^{II}(bpy^-)_3]^{-}$. Parallel spectroelectrochemical studies on substituted Ru^{II}–bipyridyl complexes have recently appeared.[2]

Tris(bipyridyl)iridium(III) $[Ir(bpy)_3]^{3+}$ (II^{3+}), in common with I^{2+}, is a low-spin $d\pi^6$ complex. However, the tervalent complex II^{3+} has relatively facile ligand reductions, and, remarkably, six successive one-electron steps are observed. The pattern of electrode potentials for II^{3+} was noted by DeArmond et al.[3] to suggest a localized-charge model for the reduced complexes II^{2+}, II^{+}, etc. We now report confirmation of this interpretation using the spectroelectrochemical methods found to be definitive for I^{2+}.

There are marked differences in the electronic spectra of isoelectronic $[Ru(bpy)_3]^{2+}$ (I^{2+}) and $[Ir(bpy)_3]^{3+}$ (II^{3+}). Whereas for I^{2+} the visible spectral region is dominated by a metal-to-ligand charge-transfer (MLCT) transition, the first prominent absorption band of II^{3+} is an intraligand $\pi\pi^*$ transition at 32 200 cm^{-1},[4] the visible and near-infrared regions of the absorption spectrum being entirely featureless. The spectra of the intermediate complexes, I^+ and I^0, are complicated in the visible region due to superposition of the Ru^{II}–bpy^0 MLCT transition and characteristic bpy^- intraligand transitions. Thus we anticipated that $[Ir(bpy)_3]^{3+}$ and its reduced analogues would prove helpful in clarifying the visible spectral region, as the bpy^- intraligand transitions should emerge from a featureless background.

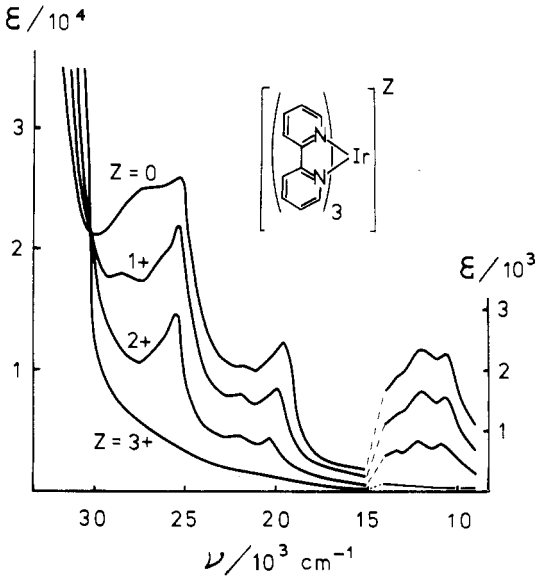


Figure 1. Absorption spectra for $[Ir(bpy)_3]^{3+/2+/+/0}$.

Results and Discussion

The reduced complexes $[Ir(bpy)_3]^{2+/+/0}$ were generated in turn in an optically transparent thin-layer electrode (OTTLE) cell, at −1.30, −1.45, and −1.60 V, respectively, vs. a nonaqueous Ag/Ag^+ reference electrode, and their spectra were measured in situ from 3500 to 33 000 cm^{-1}. In each case, after observation of the corresponding steady-state spectrum, the potential was set at −0.6 V and the spectrum was noted to return exactly to that of II^{3+} in its original concentration, thus establishing that no decomposition had occurred. In these circumstances, with strict exclusion of air, the entire series of iridium complexes proved neither solvent nor temperature sensitive, with invariant spectra in purified acetonitrile (at 30 and −40 °C), *N*,*N*-dimethylformamide, and dimethyl sulfoxide. Although $[Ir(bpy)_3]^{-}$ (II^{-}) is stable on a voltammetric time scale, it apparently decomposed on electrosynthesis. After generation of II^{-} and attempted regeneration of II^{3+} at either 15 or −40 °C, the original spectrum was not recovered, and further characterization of II^{-} (or II^{2-} and II^{3-}) was not pursued.

The successive spectra for $[Ir(bpy)_3]^{3+/2+/+/0}$ show crucial features in common with those for the ruthenium series. We see progressive growth of bands characterizing bpy^- and matching loss of the bpy^0 bands as the system is further reduced. A striking feature of Figure 1 is the maintenance of a pseudoisosbestic point relating four independent species. Thus, throughout the course of these reductions only the net interconversion of effectively isolated $Ir^{III}(bpy^0)$ and $Ir^{III}(bpy^-)$ chromophores is detected. This unequivocal observation justifies the consideration of extinction coefficients *per* ligand chromophore (see below) and establishes that the complexes should be formulated as shown in Table I. Assignment of

(1) Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *J. Chem. Soc.,, Chem. Commun.* **1981**, 287. Elsewhere,[1,6,10] we have used symbols differently for such redox sequences, e.g., I, I^-, I^{2-}, I^{3-} for $[Ru(bpy)_3]^{2+/+/0/-}$, respectively.

(2) (a) Elliot, C. M.; Hershenhart, E. J. *J. Am Chem. Soc.* **1982**, *104*, 7519. (b) Bugnon, P.; Hester, R. E., personal communication.

(3) Kahl, J. L.; Hanck, K. W.; DeArmond, K. *J. Phys. Chem.* **1978**, *82*, 540.

(4) DeArmond, M. K.; Carlin, C. M.; Huang, W. L. *Inorg. Chem.* **1980**, *19*, 62.

0020-1669/84/1323-3423$01.50/0