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Thermodynamic and Kinetic Aspects of Substituent Effects on the Redox Properties of the Carbonyl-Bridged Dirhodium Complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ and $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$

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The electrochemical reduction and oxidation of the dirhodium(I) carbonyl bridged alkyne complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ and $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ have been investigated in detail at both platinum and mercury electrodes in dichloromethane and acetonitrile. Remarkable thermodynamic and kinetic differences exist between the t-BuC$_2$-t-Bu and CF$_3$C$_2$CF$_3$ analogues. The oxidation of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ in dichloromethane produces a very stable cation, $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^+$. This complex can be generated by controlled potential electrolysis and has been examined by ESR and other techniques. The corresponding dication and monoanion are less stable on the synthetic time scale although voltammetrically they can be detected as part of the four membered redox series

$$[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^- \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} (\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$$

$$[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^{2+}$$

In contrast to data in the noncoordinating solvent dichloromethane, a considerable degree of chemical irreversibility is observed, even on the voltammetric time scale, when oxidation is achieved in acetonitrile. This is attributed to the reactions $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu]^{+/2+} + CH_3CN \xrightarrow{\text{fast}} [(\eta\text{-}C_5H_5)_2Rh_2(CO)(CH_3CN)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^{+/2+}$. These oxidized acetonitrile derivatives readily undergo further oxidation and have no inherent stability. The substitution reaction $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}RC_2R) + CH_3CN \rightleftharpoons (\eta\text{-}C_5H_5)_2Rh_2(CO)(CH_3CN)(\mu\text{-}RC_2R)$ actually occurs for the neutral complex when R = CF$_3$ and is formally an oxidative addition since a change in bonding mode of the alkyne accompanies the reaction. In contrast, no reaction with acetonitrile occurs for the neutral complex when R is the bulky t-Bu group. Substantial activation toward substitution after oxidation is therefore noted. Redox data at mercury electrodes are identical with that at platinum for the t-BuC$_2$-t-Bu species. However, formation of a mercury derivative is indicated in the electrochemistry of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ which is again consistent with the higher reactivity of the hexafluorobut-2-yne complex. In addition to a marked decrease in kinetic stability (increase in reactivity) achieved in replacement of the t-BuC$_2$-t-Bu groups by the less bulky and more electron-withdrawing CF$_3$C$_2$CF$_3$ alkyne, marked thermodynamic changes ($E_{1/2} \approx E^\circ$ values) are also found. The CF$_3$C$_2$CF$_3$ complex is harder to oxidize and easier to reduce than the t-BuC$_2$-t-Bu derivative. However, despite the fact that in the thermodynamic redox sense, $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}RC_2R_2)]^-$ is more stable when R = CF$_3$ than when R = t-Bu, the t-Bu derivative remains the more kinetically stable complex.

Introduction

A wide range of organodirhodium complexes has been synthesized in which the formal oxidation state of rhodium is either I, II, or III.[4,5] More rarely, mixed valence dirhodium complexes have been characterized (see for example, ref 6–9) with crystal structures being available in some cases. These dirhodium complexes exhibit many interesting properties. Reactivity has been examined extensively with respect to catalysis,[10] oxidative addition,[11,12] reductive elimination,[12] redox properties,[7,8,13–18] organic synthesis,[19] and photochemistry.[11] Investigation of spectroscopic properties illustrate dynamic behavior in solution

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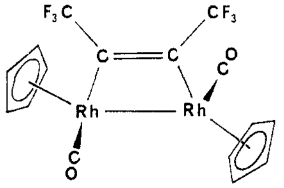
for many of the complexes (see, for example, ref 20 and 21).

The remarkable variability of structures and chemical redox properties in dirhodium chemistry is illustrated particularly well by complexes of the kind $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}RC_2R)$ and $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}RC_2R)$.

Addition of the alkyne $CF_3C_2CF_3$ to $(\eta\text{-}C_5H_5)Rh(CO)_2$ at elevated temperatures, produces $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}CF_3C_2CF_3)$.[22] The crystal structure of this compound has been determined[23] and is shown in structure I. The alkyne bridges the rhodium–rhodium bond with the two carbonyl ligands in trans positions on adjacent rhodium atoms. Formally, this is a rhodium II complex with an 18-electron configuration at each metal. A corresponding cis isomer is known, which isomerizes slowly to the trans form.[20]

In the presence of Me_3NO in dry acetone[24] structure I is converted to structure II.[25] This arrangement, in which there is a 90° twist of the alkyne and a shift of the carbonyl to a bridging position, is formally equivalent to a reductive elimination in which the 18-electron configuration is retained but the formal oxidation state of rhodium is now I. Complex II is relatively reactive and a wide range of ligands, L, add oxidatively to give the complexes $(\eta\text{-}C_5H_5)_2Rh_2(CO)L(\mu\text{-}CF_3C_2CF_3)$[11] which have structures analogous to I. Similarly, treatment of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ with diazoalkane, N_2CH_2, at 0 °C produces a μ-alkylidene complex, $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)$. At room temperature, the alkylidene group migrates to the coordinated alkyne[26] to give a mixed-valence complex in which the metals have formal oxidation states of I and II.



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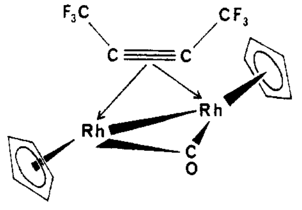

II

In the present work, the redox properties of the formally rhodium(I) species $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}RC_2R)$ (R = CF_3 or *t*-Bu) have been examined from an electrochemical viewpoint; it is shown that varying the alkyne substituent R in these carbonyl-bridged complexes has both thermodynamic and kinetic implications. It is important to develop an understanding of the effects of redox changes on the fate of bridging CO and RC_2R ligands. The significance of the bridging carbonyl group in catalysis has been emphasized by Sanger.[10] For a series of dinuclear cationic complexes of rhodium(I) $[Rh_2(\mu\text{-}X)(CO)_2(Ph_2ECH_2EPh_2]^+$ (X = Cl, Br; E = P, As), he showed that catalytical activity for the hydrogenation of alkynes to alkenes and alkenes to alkanes was related to the ease of formation of $Rh_2(\mu\text{-}CO)$ species. Other workers[27,28] have suggested that interconversions between the two alkyne bonding modes found in I and II might be an important process in catalysis.

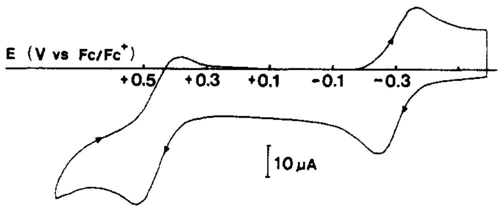

Figure 1. Cyclic voltammogram at a platinum electrode for oxidation of 0.4 mM $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ in 0.1 M TBAP in CH_2Cl_2 (scan rate = 200 mV/s; T = 20 °C).

Experimental Section

Reagents. Analytical reagent grade dichloromethane and ferrocene and HPLC-grade acetonitrile were used without further purification. The syntheses of the dirhodium complexes have been described previously.[12,22] Tetraethylammonium perchlorate (TEAP) (Southwestern Analytical Chemicals, Inc.) was dried in a vacuum desiccator. Tetra-*n*-butylammonium perchlorate (TBAP) (GFS Chemicals) was used as received.

Instrumentation. (a) Electrochemical. Working electrodes included a 4.5-mm diameter stationary platinum disk, a Beckman variable-speed rotated platinum disk, a Metrohm micrometer-style hanging mercury drop electrode, and a dropping mercury electrode mounted onto a Princeton Applied Research Corp. (PARC) 174/70 drop timer. The auxiliary electrode was a platinum wire. The reference electrode was either Ag/AgCl (acetone, saturated with dry LiCl) or $Ag/AgNO_3$ (0.01 M) in acetonitrile containing 0.1 M TEAP. Voltammetric and polarographic data were obtained by using a PARC 174A polarographic analyzer equipped with a Houston 2000 recorder or a Bioanalytical Systems BAS-100 Electrochemical Analyzer. Controlled potential electrolyses were carried out at a massive platinum gauze working electrode, using a PARC 173/179 potentiostat/digital coulometer.

(b) Electron Spin Resonance. ESR spectra were obtained with an X-band reflection-type spectrometer employing phase-sensitive detection at 100 KHz.[29] The sample was contained in a microcell which permitted in situ electrochemistry–ESR experiments.[30]

Procedure. Dirhodium complex solutions were prepared just prior to use by dissolution in acetonitrile which was 0.1 M in TEAP or in dichloromethane which was 0.1 M in TBAP. Sample solutions were protected from direct exposure to light and were deaerated with prepurified nitrogen or argon. The reference electrode was coupled to the electrochemical cell through a porous Vycor bridge which contained the same supporting electrolyte and solvent as was in the cell. In each case, the same electrochemical experiment was also performed on the same concentration of ferrocene during the same work period, and all voltages were referenced to the reversible $E^r_{1/2}$ value (approximately $E°$) for the ferrocene–ferricinium couple (Fc/Fc^+). The temperature used for measurements was (20 ± 1) °C unless otherwise stated.

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Table I. Summary of Electrochemical Oxidation Data for $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}RC_2R)_2$ Complexes

complex^a	electrode	solv	$(E_p^{ox})_1$ or $(E_{1/2}^{ox})_1$, V vs. Fc/Fc$^+$	$(\Delta E_p)_1^b$ or $(E_{3/4} - E_{1/4})_1$, mV	$(n^{ox})_1^c$	$(E_p^{ox})_2$ or $(E_{1/2}^{ox})_2$, V vs. Fc/Fc$^+$)	$(\Delta E_p)_2^b$ or $(E_{3/4} - E_{1/4})_2$, mV	$(n^{ox})_2^c$	comments
1	stat Pt^d	CH_2Cl_2	−0.256	110	1	+0.513	130	1	$(i_p^{ox})_1/(i_p^{red})_1 = 1.0$
1	stat Pt^d	CH_3CN	−0.270	100	1	+0.415	irrev^i	*g*	
1	RPDE^e	CH_2Cl_2	−0.309	57	1	0.454	61	1	
1	DME^f	CH_2Cl_2	−0.311	55	1	∼+0.4	nd^i	nd^i	second oxidation step observed as a shoulder on mercury oxidation
1	DME^f	CH_3CN	−0.320	50	1				
2	stat Pt^d	CH_2Cl_2	+0.375	150	1	+0.650	irrev^i	1	
2	stat Pt^d	CH_3CN	+0.314	irrev^i	*g*		irrev^i		complex reacts with CH_3CN^h
2	RPDE^e	CH_2Cl_2	+0.286	94	1	+0.629	115	1	
2	DME^f	CH_2Cl_2	+0.189	75	2				
2	DME^f	CH_3CN							no wave; complex reacts with CH_3CN^h
2	HMDE^d	CH_2Cl_2	∼+0.24	irrev^i	g				

[a] 1, $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$; **2**, $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$; concentration = 0.4 mM; T = 20 °C. [b] For 0.4 mM Fc: $(E_p^{ox}) - (E_p^{red})$ = 110–150 mV at v = 200 mV/s. [c] Based on comparison with limiting current for $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ where n is known to be 1. [d] Scan rate = 200 mV/s. [e] Scan rate = 10 mV/s; rotation speed = 25 rps. [f] Drop time = 1 s. [g] Multielectron process. [h] Complex reacts with CH_3CN, presumably to form $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CH_3CN)(\mu\text{-}CF_3C_2CF_3)$. See ref 33. [i] nd = not determined for reason stated in comments column; irrev = irreversible electrode process.

Results and Discussion

(i) Electrochemical Oxidation of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ in Dichloromethane. Electrochemical data for oxidation of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ are summarized in Table I. Figure 1 shows a cyclic voltammogram at a platinum electrode in dichloromethane. Two well-separated processes are observed. The first oxidation step is both chemically and electrochemically reversible based upon the peak-to-peak separation (identical with oxidation of ferrocene) and ratio of oxidative (forward scan) to reductive peak height (reverse scan). The calculated reversible $E^r_{1/2}$ value of −0.31 V vs. Fc/Fc$^+$ indicates that oxidation of this compound requires only mild conditions. The second oxidation process has the same oxidative peak current as the first oxidation step but is not completely reversible in the chemical sense at a scan rate of 200 mV/s at 20 °C. The calculated $E^r_{1/2}$ value of approximately 0.45 V vs. Fc/Fc$^+$ indicates that removal of a second electron from the complex should also be relatively easily achieved. At faster scan rates or lower temperatures the second oxidation process is chemically reversible, but the peak-to-peak separation for oxidation and reduction peaks departs slightly from the value expected for a nernstian response.

Oxidative voltammetry at a rotating platinum disk electrode, RPDE, is shown in Figure 2a. Two consecutive oxidation waves of equal height with $(E_{3/4} - E_{1/4})$ values of 57 and 61 mV, respectively, are observed. Data at RPDE are consistent with both processes being essentially diffusion controlled.

Controlled potential electrolysis at 0.1 V vs. Fc/Fc$^+$ corresponding to the limiting current region of the first oxidation step goes rapidly to completion. Subsequent voltammetry at the RPDE (Figure 2b) demonstrated that after correction for Ohmic iR drop the entire current–voltage curve had merely shifted on the current axis, so that the original first oxidation process is now a reduction process with an identical $E_{1/2}$ value to that before oxidation while the second step remained as an oxidation process (compare parts a and b of Figure 2). Subsequent reductive electrolysis at −1.1 V vs. Fc/Fc$^+$ restored the solution to its initial composition (100% yield) as evidenced by subsequent voltammetry which gave curves identical with those in Figure 2a. This cyclical oxidative and reductive electrolysis was repeated at least six times on each of two samples without apparent chemical degradation of the nitrogen-purged, light-excluded samples over a period of nearly an hour. Coulometry during each step of the cyclic electrolysis experiments gave n values of 0.89 ± 0.04. This data, obtained on dilute solutions (5×10^{-5} M), is not highly accurate. However, in conjunction with the shape of cyclic and RPDE voltammograms the data demonstrate that oxidation of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ involves two consecutive one-electron oxidation steps

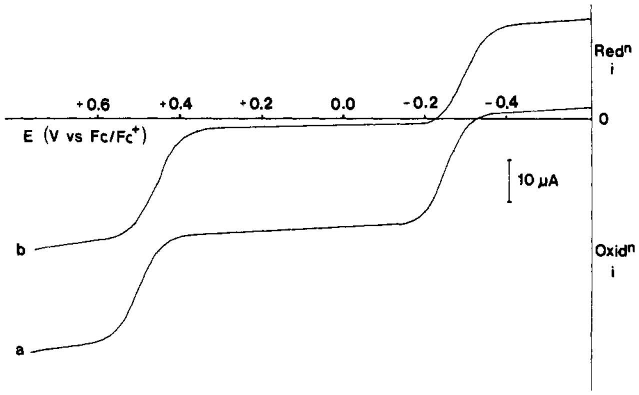

Figure 2. Voltammograms at a rotated platinum disk electrode for oxidation of $(\eta\text{-}(C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ in 0.1 M TBAP in CH_2Cl_2 (scan rate = 10 mV/s; rotation rate = 25 rps): (a) before electrolysis; (b) after electrolysis at +0.10 V vs. Fc/Fc$^+$ (T = 20 °C).

$$(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu) \xrightleftharpoons{(E_{1/2})_1} [(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^+ + e^- \quad (1)$$

$$[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^+ \xrightleftharpoons{(E_{1/2})_2} [(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^{2+} + e^- \quad (2)$$

$$(E_{1/2})_1 = -0.31 \text{ V vs. Fc/Fc}^+; \quad (E_{1/2})_2 = +0.45 \text{ V vs. Fc/Fc}^+$$

Equation 1 represents the formation of a stable radical monocation in which rhodium has a formal oxidation state of 1.5. An ESR spectrum of the species assigned the formula $[(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^+$ was obtained. This spectrum was obtained by controlled potential electrolysis in situ to an ESR spectrometer. The g value of 2.046 and line width of 32.4 and 20.0 G at −73 and 6 °C, respectively, may be compared to the values of 2.00 and 10 G reported for $[Rh_2(\mu\text{-}dpm)_2(1,2\text{-}O_2C_6Cl_4)(CO)]^+$ (dpm = bis(diphenylphosphino)methane),[14] although this latter compound does not have a bridging carbonyl and the odd

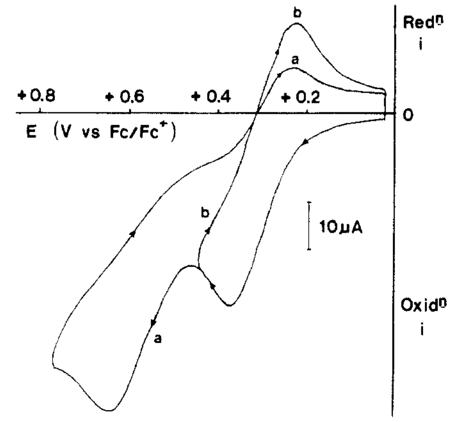

Figure 3. Cyclic voltammograms at a platinum electrode for oxidation of 0.4 mM $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ in 0.1 M TBAP in CH_2Cl_2 (scan rate = 200 mV/s; T = 20 °C): (a) sweep reversal after second oxidation peak; (b) sweep reversal after first oxidation peak.

electron is believed to be localized on the semiquinone ligand. No hyperfine coupling was observed with rhodium.

Controlled potential electrolysis at +0.7 V vs. Fc/Fc^+ (limiting current region of the second oxidation wave) was slow. Coulometric monitoring produced a relative n value in the range of 3.5–4 and 2.5–3 when the complex had been preoxidized at +0.1 V vs. Fc/Fc^+.

Clearly, a complicated second oxidation process occurs on the electrochemical synthetic time scale, even though short time scale voltammetry is consistent with the formation of $[(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^{2+}$ as per eq 2. This complex may formally be regarded as a Rh(II) species. The overall process in the preparative time scale is probably

$$\text{Rh(I)–Rh(I)} \rightarrow 2\text{Rh(III)} + 4e^- \qquad (3)$$

with $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^{2+}$ being an unstable intermediate.

On mercury electrodes one well-defined oxidation wave at the same potential as at platinum is observed under conditions of cyclic voltammetry at a hanging mercury drop electrode or polarography at the dropping mercury electrode. The second oxidation process merges with the potentials limit available in mercury electrodes. Data contained in Table I indicate that the nature of the electrode (platinum or mercury) does not influence the electrochemistry of the *tert*-butyl complex.

(ii) Oxidation of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ in Dichloromethane. Spectroscopic data indicate that $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ and $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ are structurally analogous. However, changing the alkyne substituent exerts a profound influence on the thermodynamic and kinetic aspects of the electrochemical oxidation in dichloromethane. Data for oxidation of both complexes are contained in Table I. It can be seen that the presence of $CF_3C_2CF_3$ causes the first oxidation process to shift to considerably more positive potentials, as well as significantly decreasing the stability of the cation $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)]^+$ and its dication $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)]^{2+}$. The separation in $E_{1/2}$ between the two oxidation steps is also decreased, but since the $E_{1/2}$ value for the second oxidation process no longer has thermodynamic significance, the origin of this effect is unclear. Figure 3 shows a cyclic voltammogram for the $CF_3C_2CF_3$ derivative which should be compared with Figure 1 to illustrate the considerable differences between the two complexes.

Chemically, $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ is known to be more reactive than $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$. In the presence of carbon monoxide or other ligands, L, the $CF_3C_2CF_3$ compound readily adds another ligand to give $(\eta\text{-}C_5H_5)_2Rh_2(CO)(L)(\mu\text{-}CF_3C_2CF_3)$. This is effectively an oxidative addition to form a rhodium(II) complex as noted earlier, because the coordinated alkyne twists 90° after addition of the ligand[12] (compare structures I and II). In contrast, $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ is inert toward substitution reactions of this kind.

The reactivity difference also seems to be emphasized after oxidation. The first oxidation step at short voltammetric time scales in CH_2Cl_2 can be ascribed to the process

$$(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3) \rightleftharpoons [(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)]^+ + e^- \quad (4)$$

where in longer time scale experiment the reaction

$$[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)]^+ \rightarrow \text{products} \qquad (5)$$

must be taken into account. The origin of differences in stability of the cation is presumably a combination of kinetic and thermodynamic effects. Thermodynamically, $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^+$, being generated at about 500 mV less positive than $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)]^+$, is therefore more stable in the redox sense. Coupled with this, $t\text{-}BuC_2\text{-}t\text{-}Bu$ contains the bulky t-Bu groups which presumably inhibit rapid inter- and intramolecular reactions involving a 90° twist of the alkyne that occur when the less bulky $CF_3C_2F_3$ group is present.

While $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)]^+$ has some stability (cyclic voltammograms for the first oxidation steps are chemically reversible at a scan rate of 5 V s^{-1} at 20 °C), no direct electrochemical evidence for $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)]^{2+}$ can be obtained with scan rates as fast as 50 V s^{-1}. This species is also considerably less stable than the analogous $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^{2+}$ complex, and the same order of stability applies in all formal oxidation states of the series $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}RC_2R)]^{0/1+/2+}$.

Controlled potential electrolysis and coulometric monitoring of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ at the limiting current region of the first wave (0.4 V vs. Fc/Fc^+) gave an apparent n value of 2.6 ± 0.4. On the limiting current region of the second wave, an experimental n value of 3.6 ± 0.4 was obtained. Voltammetry subsequent to electrolysis gave no well-defined curves, and the bright green sample solution became yellow after electrolysis irrespective of the potential. Unfortunately, the products of controlled potential oxidative electrolysis have not been characterized, but they are probably formally rhodium(III) compounds.

In situ electrolysis at a platinum microelectrode in an ESR spectrometer at low temperatures enables the ESR spectrum of $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)]^+$ to be obtained. At −33 °C a single-line spectrum with a g value of 2.057 is obtained with a line width of 30.0 G. No hyperfine coupling of rhodium or fluorine is observed.

The enhanced reactivity of the $CF_3C_2CF_3$ complex compared to the *tert*-butyl derivative in different formal oxidation states is also illustrated by the specific electrode dependence on mercury which was not observed for $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$. Thus, $E_{1/2}$ on the mercury electrode (Table I) is less positive than on platinum for $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$. Furthermore, at a mercury electrode, the process is irreversible and the limiting current per unit concentration is larger than for $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$. The different $E_{1/2}$ values at platinum and mercury electrodes are readily explained if it is assumed that mercury is intimately involved in the process at mercury electrodes for oxidation

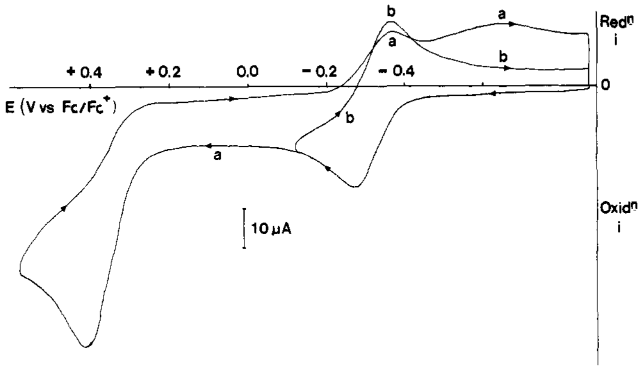

Figure 4. Cyclic voltammograms at a platinum electrode for oxidation of saturated (approximately 0.3 mM) $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)$ in 0.1 M TEAP in CH_3CN (scan rate = 200 mV/s; T = 20 °C): (a) sweep reversed after second oxidation peak; (b) sweep reversed after first oxidation peak.

of $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-CF_3C_2CF_3)$. The initial product formed at mercury is probably the highly reactive species $[Hg\{(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-CF_3C_2CF_3)\}_2]^{2+}$ (see eq 6). This

$$Hg + 2(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-CF_3C_2CF_3)_2 \rightleftharpoons [Hg\{(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-CF_3C_2CF_3)\}_2]^{2+} + 2e^- \quad (6)$$

compound presumably rapidly rearranges to give the observed chemically overall irreversible process. Connelly et al.[13] have noted the formation of what is probably a closely related analogue $[Ag\{(\eta-C_5H_5)Rh(CO)(PPh_3)\}_2]^+$ by reaction of $(\eta-C_5H_5)Rh(CO)(PPh_3)$ with $AgPF_6$.

Interaction between mercury and the dirhodium complex is not unexpected. Reaction of $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-Ph_2PCH_2PPh_2)$ with $HgCl_2$ is known[31] to produce $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-Ph_2PCH_2PPh_2)(\mu-HgCl_2)$ and oxidation of *trans*-$RhCl(CO)(PPh_2R)_2$ (R = Et, $CHMe_2$, CH_2SPh) also produces rhodium–mercury bonded complexes.[32] Moreover, we have observed an immediate reaction between $(\mu-C_5H_5)_2Rh_2(\mu-CO)(\mu-CF_3C_2CF_3)$ and mercuric acetate to produce a red-brown solution with terminal carbonyl absorption at 2020 and 2000 cm⁻¹ in the infrared spectrum.

(iii) Electrochemical Oxidation of $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-RC_2R)$ in Acetonitrile. The first one-electron oxidation process for $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)$ is only slightly affected in the thermodynamic sense by change from the noncoordinating solvent dichloromethane to the more strongly coordinating acetonitrile. However, in acetonitrile, the first oxidation step is no longer completely reversible in the chemical sense at slow scan rates, since the ratio of $(i_p)^{ox}/(i_p)^{red}$ is less than unity under conditions of cyclic voltammetry. Unfortunately, $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)$ is only sparingly soluble in CH_3CN (~0.3 mM), and data at fast scan rates suffer from a relatively poor faradaic-to-changing current ratio. However, within experimental error, the first oxidation step is completely reversible in the chemical sense at a scan rate of 5 V/s. In CH_3CN the second oxidation step, unlike the case in CH_2Cl_2, is completely irreversible and is a multielectron process as shown in Figure 4. Data imply that CH_3CN attacks $[(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)]^+$ relatively slowly and $[(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)]^{2+}$ rapidly whereas no reaction is observed over a period of at least 1 h for the parent species $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)$. Apparently the rate of attack by CH_3CN increases in proportion to the degree of oxidation.

The different degree of reactivity of the $CF_3C_2CF_3$ and $t-BuC_2-t-Bu$ analogues is highlighted by the reaction with acetonitrile. Voltammetric studies in CH_3CN of $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-CF_3C_2CF_3)$ are time dependent, and the characteristic green color exhibited in CH_2Cl_2 is replaced by a yellow color. Reaction 7 occurs in acetonitrile

$$(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-CF_3C_2CF_3) + CH_3CN \rightleftharpoons (\eta-C_5H_5)_2Rh_2(CO)(CH_3CN)(\mu-CF_3C_2CF_3) \quad (7)$$

at 20 °C[33] to give a nonbridged carbonyl complex which gives rise to a single irreversible multielectron oxidation wave at +0.314 V vs. Fc/Fc⁺. Limiting current data suggest that this is either a two- or three-electron process:

$$(\eta-C_5H_5)_2Rh_2(CO)(CH_3CN)(\mu-CF_3C_2F_3)_2 \rightarrow [\text{products}]^{x+} + xe^- \quad (8)$$

The electrochemistry of $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)$ in CH_3CN is therefore connected with activation of the substitution reaction, and the first oxidation step at slow scan rates can be assigned as follows:

$$(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu) \rightleftharpoons [(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)]^+ + e^- \quad (9a)$$

$$[(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)]^+ + CH_3CN \xrightarrow{\text{slow}} [(\eta-C_5H_5)_2Rh_2(CO)(CH_3CN)(\mu-t-BuC_2-t-Bu)]^+ \rightarrow \text{electroactive products} \quad (9b)$$

Equation 9b does not occur at scan rates in excess of 5 V/s under conditions of cyclic voltammetry in CH_3CN. However, even in this time domain $[(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu]^{2+}$ is attacked by CH_3CN so that the second oxidation process is described by the following multielectron process:

$$(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu) \rightleftharpoons [(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)]^+ + e^- \quad (10a)$$

$$[(\eta-C_5H_5)_2Rh_2(\mu-CO)(t-BuC_2-t-Bu)]^+ \rightleftharpoons [(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)]^{2+} + e^- \quad (10b)$$

$$[(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)]^{2+} + CH_3CN \rightarrow [(\eta-C_5H_5)_2Rh_2(CO)(CH_3CN)(\mu-t-BuC_2-t-Bu)]^{2+} \quad (10c)$$

$$[(\eta-C_5H_5)_2Rh_2(CO)(CH_3CN)(\mu-t-BuC_2-t-Bu)]^{2+} + CH_3CN \rightarrow [\text{products}]^{x+} + (x-2)e^- \quad (10d)$$

The overall equation for the second process can therefore be written as

$$[(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-t-BuC_2-t-Bu)]^+ \xrightarrow{CH_3CN} [\text{products}]^{x+} + (x-1)e^- \quad (10e)$$

In CH_3CN a reversible diffusion-controlled one-electron oxidation wave is observed at mercury electrodes for the $t-BuC_2-t-Bu$ derivative as was the case in CH_2Cl_2. However, the limiting current per unit concentration is enhanced for the oxidation process of the $CF_3C_2CF_3$ analogue at mercury electrodes, implying the interaction of both mercury and the solvent.

(iv) Electrochemical Reduction of $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-RC_2R)$. Table II summarizes electrochemical data

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[31] Faraone, F.; LoSchiavo, S.; Bruno, G.; Bombieri, G. *J. Chem. Soc., Chem. Commun.* **1984**, 6.

[32] Sanger, A. R. *Can. J. Chem.* **1984**, *62*, 822.

[33] The ¹H NMR spectrum of a solution of $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-CF_3C_2CF_3)$ in CD_3CN shows a single resonance for the C_5H_5 protons at δ 5.48. However, the IR spectrum of the solution shows peaks at 1980 m and 1840 s cm⁻¹ assigned to terminal and bridging carbonyls respectively. These data can be rationalized in terms of rapid establishment of the equilibrium and rapid scrambling of the CO and NCR ligands in the substituted complex. Only $(\mu-C_5H_5)_2Rh_2(\mu-CO)(\mu-CF_3C_2CF_3)$ is recovered when acetonitrile is evaporated from the solution.

Table II. Summary of Electrochemical Reduction Data for $(\eta\text{-}C_5H_2)_2Rh_2(\mu\text{-}CO)(\mu\text{-}RC_2R)$ Complexes

complex[a]	electrode	solv	$(E_p^{red})_3$ or $(E_{1/2}^{red})_3$, V vs. Fc/Fc$^+$	$(\Delta E_p)_3$[b] or $(E_{1/4} - E_{3/4})_3$, mV	comments
1	stat Pt[d]	CH_2Cl_2	~−2.7	nd[h]	shoulder on solvent red. limit
1	stat Pt[d]	CH_3CN	−2.34	120	
1	DME[f]	CH_2Cl_2	~−2.5	nd[h]	merged with solvent red. limit
1	DME[f]	CH_3CN	~−2.4	nd[h]	close to solvent red. limit
2	stat Pt[d]	CH_2Cl_2	−1.840	irrev[h]	reversible at faster scan rates
2	stat Pt[d]	CH_3CN[g]	−1.629	98	complex reacts with CH_3CN
2	RPDE[e]	CH_2Cl_2	−1.848	134	
2	DME[f]	CH_2Cl_2	−1.512	72	
2	DME[f]	CH_3CN[g]	−1.528	60	complex reacts with CH_3CN; second wave observed with $(E_{1/2}^{red}) = -1.78$ V and $E_{1/4} - E_{3/4} = 55$ mV
2	HMDE[d]	CH_2Cl_2	−1.855	irrev[h]	
2	HMDE[d]	CH_3CN[g]	−1.567	irrev[h]	complex reacts with CH_3CN; second reduction wave observed with $(E_p^{red}) = -1.79$ V and $(\Delta E_p) = 50$ mV

[a] 1, $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$; **2**, $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$; concentration = 0.4 mM; $T = 20$ °C. [b] For 0.4 mM Fc: $(E_p^{ox}) - (E_p^{red}) = 110\text{–}150$ mV at $v = 200$ mV/s. [c] Based on comparison with oxidation current seen for $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$. [d] Scan rate = 200 mV/s. [e] Scan rate = 10 mV/s; rotation speed = 25 rps. [f] Drop time = 1 s. [g] Complex reacts with CH_3CN, presumably to form $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CH_3CN)(\mu\text{-}CF_3C_2F_3)$. See ref 33. [h] nd = not determined for reason stated in comments column; irrev = irreversible electrode process.

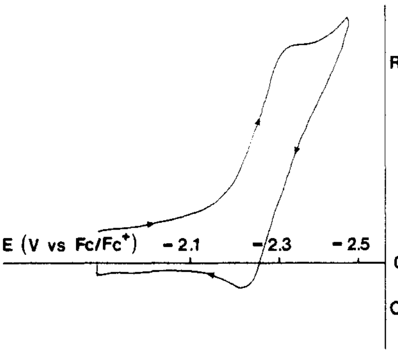

Figure 5. Cyclic voltammogram on a platinum electrode for reduction of saturated (approximately 0.3 mM) $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ in 0.1 M TBAP in CH_3CN (scan rate = 200 mV/s; $T = 20$ °C).

for reduction of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ and $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ at platinum and mercury electrodes in CH_2Cl_2 and CH_3CN. In most cases, the reduction processes contain substantial complexity. The reduction of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)$ in CH_2Cl_2 occurs near the solvent limit and cannot be adequately characterized. However, in CH_3CN, which has a wider available potential range, a well-defined chemically and electrochemically reversible process is observed at moderate scan rates at platinum electrodes as shown in Figure 5. This process is assigned to the formation of the anion $[(\eta\text{-}(C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^-$ as in eq 11. In

$$(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu) + e^- \overset{(E_{1/2})_3}{\rightleftharpoons} [(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}t\text{-}BuC_2\text{-}t\text{-}Bu)]^- \quad (11)$$

$$(E_{1/2})_3 = -2.28 \text{ V vs. Fc}|\text{Fc}^+$$

contrast, while reduction of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ occurs at considerably less negative potentials than for the $t\text{-}BuC_2\text{-}t\text{-}Bu$ complex, the product of reduction is unstable even in the noncoordinating solvent dichloromethane on the time scale of cyclic voltammetry when a scan rate of 200 mV/s is used (Figure 6). With this time domain, the process occurs as an overall irreversible two-electron reduction step. By contrast, at scan rates of 50 V/s this process has a considerable degree of chemical reversibility and is observed as a one-electron reduction process, implying that $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)]^-$ has at least limited stability. At short time domains the reduction process can be written as

$$(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3) + e^- \rightleftharpoons [(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)]^-$$

with the reaction

$$[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)]^- \rightarrow \text{electroactive product}$$

occurring in longer time domain experiments. Overall the reduction process corresponds to the process

$$(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3) + 2e^- \rightarrow \text{products}$$

The irreversible reduction of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ is a multielectron step in CH_2Cl_2 under polarographic conditions again illustrating that the electrode plays an important role in the electrochemistry at mercury electrodes. Reduction processes of this complex in acetonitrile were again time dependent because of the specific reaction with the solvent described elsewhere (eq 6). In summary, the species $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}RC_2R)]^-$ is more stable when R = t-Bu than CF_3, despite the fact that in the thermodynamic sense it should be more reactive, being reduced at more negative potentials. Furthermore, the anion does not have the inherent stability associated with the cation $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}RC_2R)]^+$.

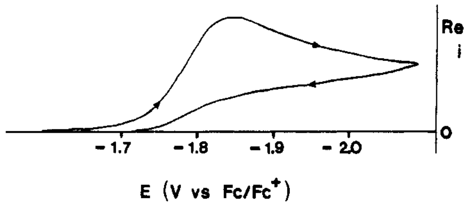

Figure 6. Cyclic voltammograms at a platinum electrode for reduction of 0.4 mM $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ in 0.1 M TBAP in CH_2Cl_2 (scan rate = 200 mV/s; $T = 20$ °C).

Conclusions

Carbonyl-bridged dimers of the kind $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}RC_2R)$ can exist as part of a four-member redox series involving the complexes $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}RC_2R)]^{1-/0/+/2+}$. The thermodynamic and kinetic stability of the complexes is markedly dependent on the substituent R. When R = t-Bu, the complexes are considerably easier to oxidize but harder to reduce than when R = CF_3. In contrast, irrespective of the thermodynamic stability, all of the anionic, cationic, and neutral complexes are kinetically more stable in the presence of the sterically bulky *t*-Bu group than with R = CF_3. The ability of the bridged carbonyl configuration to be retained during electron-transfer reactions of dirhodium complexes may be significant in their potential role as catalysts since the bridging format has been postulated to be essential in this role in other studies.[10] The ability of $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}R_2C_2R)]^{1-/0/+1/2+}$ complexes to participate in catalytic processes will be investigated in future work in these laboratories.

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Cobalt–Rhodium Heptacarbonyl: A Coordinatively Unsaturated Dinuclear Metal Carbonyl

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$CoRh(CO)_7$ (**3**) was prepared by the reaction of $Na[Co(CO)_4]$ with $[Rh(CO)_2Cl]_2$ under a continuous purge of carbon monoxide at −78 °C or by the treatment of $Co_2Rh_2(CO)_{12}$ (**4**) with 2.5 bar of CO at 0 °C. The $CoRh(CO)_7$ formula for **3** was established on the basis of its decomposition with Br_2/CH_2Cl_2 and I_2/pyridine followed by atomic emission analysis of the metals and freezing point molecular weight determination under carbon monoxide pressure. Its yellow crystals or its *n*-hexane solutions are stable only below −65 °C under N_2. Under carbon monoxide the existence of two pseudoequilibria is observed: between $CoRh(CO)_7$ (**3**) and $Co_2Rh_2(CO)_{12}$ (**4**) ($-65\ °C < T < 15\ °C$ and $0 < p_{CO} < 2.5$ bar) and between $CoRh(CO)_7$ (**3**) and $CoRh(CO)_8$ (**5**) ($T = 0\ °C$ and $130 < p_{CO} < 160$ bar), respectively. At room temperature and under 10 bar of CO pressure **3** disproportionates very slowly to $Co_2(CO)_8$ (**1**) and $Rh_4(CO)_{12}$ (**2**).

Introduction

Neutral dinuclear metal carbonyls containing only carbonyl ligands are the simplest models for understanding metal–metal interactions and subsequent reactions, which involve the participation of two metal centers. Whereas the chemistry of homodinuclear carbonyls is well documented,[1] the field of mixed-metal dinuclear carbonyls is not as extensively studied.[2]

First, $CoMn(CO)_9$[3] and subsequently the other $CoM(CO)_9$ compounds (M = Re,[4] Tc[5]) were prepared. Furthermore, all three $MM'(CO)_{10}$ species (M or M′ = Mn, Tc, Re)[6,7] have been obtained and characterized.[6-8] It is striking that although several higher nuclearity mixed-metal carbonyls, $M_3M'(CO)_{12}$ and $M_2M'_2(CO)_{12}$ (M or M′ = Co, Rh, Ir), within the cobalt triad had been reported,[9] no dinuclear M–M′ carbonyls were known in this group until recently.

The existence of a $Co_xRh_y(CO)_z$ species, different from those known hitherto, was first suggested by the synergism observed in the combined application of $Co_2(CO)_8$ (**1**) and $Rh_4(CO)_{12}$ (**2**) as catalyst precursors in the hydrocarbonylation of diketene.[10] During the search for the origin of the synergetic effect it was shown that **1** reacts with **2** under carbon monoxide pressure, in the temperature range between 40 and 85 °C to form a mixed-metal carbonyl formulated as $CoRh(CO)_7$ (**3**).[11] Although **3** had not been isolated in that study, its formula and possible structure were proposed on the basis of the stoichiometry of its formation and its IR spectrum and solubility. The $CoRh(CO)_7$ formula implied a coordinative unsaturation in this molecule, which was assumed to be related mainly to the relative stability of the square-planar 16-electron configuration of the rhodium atom.[11]

Considering the unprecedented structural feature for a nonsubstituted metal carbonyl like **3** and its possible role in cobalt–rhodium catalytic systems, a more detailed study was aimed at the preparation, isolation, and characteri-

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