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Rearrangement Mechanisms in Slipped Triple-Decker Complexes of Cobalt and Rhodium

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Intramolecular rearrangements in $[Cp_2Rh_2(Cot)]^{2+}$ and $[Cp^*{}_2Co_2(Cot)]^{2+}$ (Cp = cyclopentadienyl; Cp* = pentamethylcyclopentadienyl; Cot = cyclooctatetraene) in solution were studied by line-shape analyses of their variable-temperature ^1H NMR spectra. The rearrangement mechanisms are different for these isostructural transoid bimetallic complexes, both of which have a bridging Cot ligand. The predominant rearrangement pathway for the rhodium complex involves a 1,3-shift of one metal at a time along the Cot ring periphery with a free energy of activation (ΔG^*) of 14.5 kcal/mol, whereas the cobalt complex rearrangement involves 1,2-shifts of both metals (ΔG^* = 14.0 kcal/mol). A transition state with a true "triple-decker" structure is ruled out by these studies.

Introduction

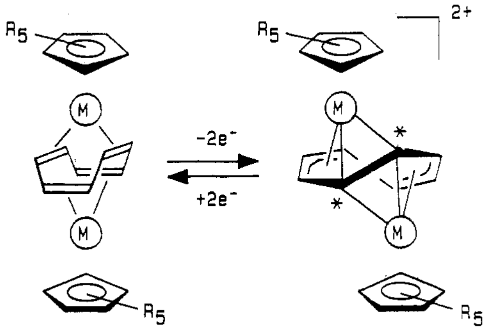
Complexes in which metals are bonded to either side of a polyolefin are of special interest insofar as they relate to "triple-decker" sandwich structures.[1] To date just two such complexes containing only carbons in the central ring have been reported, namely, $[Cp_2Ni_2(C_5H_5)]^+$ (Cp = η^5-C_5H_5)[2] and $Cp_2V_2(C_6H_6)$.[3] For this reason, "near-miss" triple-decker complexes[1] with metals bonded to the nonaromatic hydrocarbon cyclooctatetraene (Cot) have received attention, with attempts being made to alter the dimetallic C_8H_8 structure by oxidation[4] or reduction[5] of the neutral complexes. The dicationic species $[Cp_2M_2(C_8H_8)]^{2+}$ (M = Co,[4a] Rh[4b]) and $[Cp^*{}_2Co_2(C_8H_8)]^{2+}$ (Cp* = η^5-C_5Me_5)[4b] were reported by us earlier and have the "slipped" triple-decker structure shown below.

These and related complexes are fluxional.[4b,5] Given the general interest in their structure,[1,5] we thought that a study of their rearrangement pathways by dynamic NMR (DNMR) spectroscopy would be of interest. DNMR studies of dinuclear complexes of large hydrocarbons have apparently been previously restricted to complexes in which the metals are cisoid,[6] in contrast to the transoid structures of the present complexes.

In the present work, the fluxionality of the transoid complexes $[Cp^*{}_2Co_2(C_8H_8)]^{2+}$ and $[Cp_2Rh_2(C_8H_8)]^{2+}$ has been studied in detail. We find that in the dicobalt complex the metals move in a series of 1,2-shifts on the Cot ring but that 1,3-shifts are found for the dirhodium complex. One of the goals of this research was to determine if the transition state for rearrangement possessed a true triple-decker structure.[7] Such a transition state is ruled out by our data.

Results and Discussion

I. Structural Information. The possibility of isolating the dicationic complexes emerged from our earlier electrochemical studies[4] which showed that the neutral bimetallic complexes $Cp_2Co_2(Cot)$ (Cp = cyclopentadienyl, Cot = cyclooctatetraene, M = Co,[8a] M = Rh[8b]) and $Cp^*{}_2Co_2(Cot)$[8c] (Cp* = pentamethylcyclopentadienyl), in which the Cot is η^4-bonded to each metal atom through alternate double bonds, undergo two-electron oxidation.



M = Rh, R = H
M = Co, R = Me

The dicationic dicobalt compound $[Cp_2Co_2(Cot)]^{2+}$ could not be isolated due to thermal instability. In the case of dirhodium complex, the dication was isolated and its structure determined by X-ray diffraction.[4b] Oxidation changes the bridging cyclooctatetraene from a bis η^4- to a bis η^5-ligand since the metal atoms now share two adjacent carbon atoms (see positions with an asterisk in drawing). The dication possesses C_2 symmetry in which the symmetry axis passes through the midpoint of the Cot C1–C2 bond shared by both metal atoms and the C5–C6 bond. The bridging Cot has two planar four-carbon fragments that are twisted with respect to each other by 34.8°. Oxidation of the Cp*Co analogue yielded a stable dicationic complex which was isolated as dark brown crystals. Slow-exchange ^1H NMR spectra for both compounds were obtained below 240 K (vide infra) and are completely analogous. Thus, the dicobalt complex is assumed to have a ground-state structure identical with that of the dirhodium compound. Above 240 K, Cot proton NMR signals of both $[Cp_2Rh_2(Cot)]^{2+}$ and $[Cp_2{}^*Co_2(Cot)]^{2+}$ broaden and coalesce, but in a different manner, suggesting different rearrangement pathways for magnetization transfer among protons of the bridging Cot ligand.

II. Assignment of ^1H NMR Resonances. $[Cp_2Rh_2(Cot)]^{2+}$. The ^1H NMR spectrum (250 MHz) of the di-

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[1] Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

[2] Dubler, E.; Textor, M.; Oswald, H. R.; Salzer, A. *Angew. Chem.* **1974**, *86*, 125.

[3] Duff, A. W.; Jonas, K. *J. Am. Chem. Soc.* **1983**, *105*, 5479.

[4] (a) Moraczewski, M.; Geiger, W. E. *J. Am. Chem. Soc.* **1978**, *100*, 7429. (b) Edwin, J.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 3052.

[5] Bieri, J. H.; Egolf, T.; von Philipsborn, W.; Piantini, U.; Prewo, R.; Ruppli, U.; Salzer, A. *Organometallics* **1986**, *5*, 2413.

[6] For a general review of fluctional processes in cyclooctatetraene complexes see: Mann, B. E. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1982; Vol. 3, pp 131–147.

[7] I.e., a structure with a planar Cot ring and metals symmetrically disposed along its C_8 axis.

[8] (a) Fritz, H. P.; Keller, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biol.* **1961**, *16B*, 348. (b) Brenner, K. S.; Fischer, E. O.; Fritz, H. P.; Kreiter, C. G. *Chem. Ber.* **1963**, *96*, 2632. (c) Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1985**, *23*, 15.

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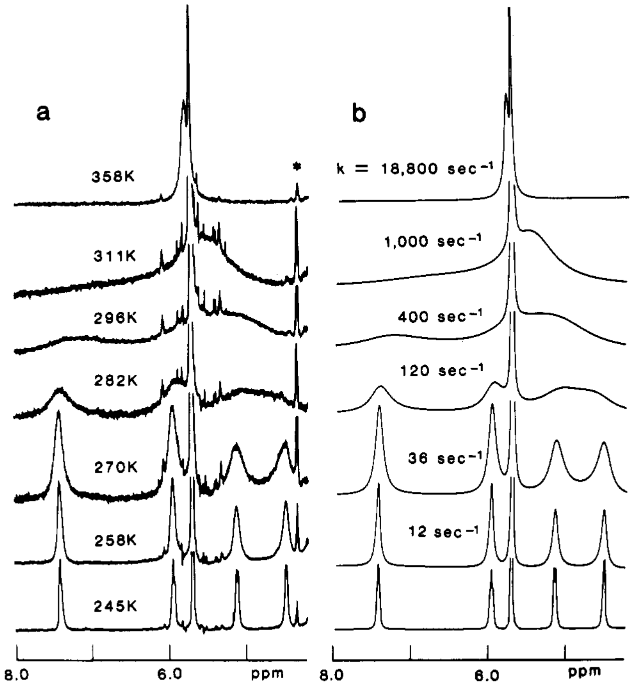
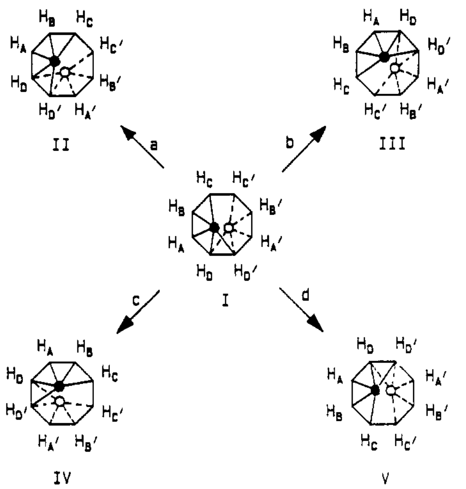


Figure 1. (a) Experimental ^1H NMR spectra of $[Cp_2Rh_2(Cot)]^{2+}$. The peak marked with an asterisk is a side-band of CHD_2NO_2. (b) Calculated spectra based on 1,3-metal shift of any one metal (pathway b in Scheme I).

rhodium complex in CD_3NO_2 at 358 K shows a sharp singlet for the Cp protons at δ 5.70 and an exchange broadened singlet for the Cot protons at δ 5.80. All chemical shifts are referred to CHD_2NO_2 at δ 4.05.[13] At lower temperatures, the Cp singlet remains sharp and unchanged as low as 245 K (Figure 1). In contrast, the Cot resonance decoalesces and, at 245 K, is separated into four signals of equal area at δ_A 7.46, δ_B 5.98, δ_C 5.10, and δ_D 4.57. The observation of just four resonances is consistent with the C_2 symmetry of the dication. We achieved an acceptable theoretical simulation of the spectrum at 245 K by using a four-spin model with $J_{AB} = J_{AD} = 4.5$ Hz, $J_{BC} = 6.1$ Hz, $J_{AC} = J_{BD} = 0.7$ Hz, and $J_{CD} = 0.0$ Hz (Figure 1, bottom trace).

Assignment of NMR chemical shifts to the Cot protons is essential in order to derive the intramolecular exchange itinerary from theoretical DNMR line-shape simulations (vide infra). Chemical shifts were assigned on the basis of the assumption that the proton on a carbon atom which is bonded to both metal atoms in the dicationic dirhodium compound is the most shielded of all protons and therefore shows up at the lowest frequency, i.e., at δ_D 4.57. Coherent irradiation experiments make further chemical shift assignments straightforward. Irradiation of the signal at δ_D 4.57 causes the collapse of the "triplet" at δ_A 7.56 into a "doublet" and no dramatic changes in any other resonance. Thus, H_D is adjacent to H_A (see structure I in Scheme I); $H_{D'}$ is adjacent to $H_{A'}$. H_A and $H_{A'}$ can be interchanged by a C_2 symmetry operation and are equivalent. The same is true for H_D and $H_{D'}$, H_B and $H_{B'}$, and H_C and $H_{C'}$. Irradiation of the signal at δ_A 7.46 causes the resonances at δ_B 5.98 and δ_D 4.57 to collapse, respectively, into a doublet and a singlet. Therefore, H_A is adjacent to H_B and H_D. Irradiation at δ_B 5.98 causes the signals at δ_A 7.46 and δ_C 5.10 to collapse, respectively, into a doublet and a singlet. H_A and H_C are adjacent to H_B. Irradiation at δ_C 5.10 causes only the signal at δ_B 5.98 to collapse into a doublet. H_C is adjacent to H_B and $H_{C'}$ (Scheme I). Thus, one subset of NMR-distinguishable protons on the Cot ring must be ordered in the sequence H_D–H_A–H_B–H_C. If our assumption regarding the assignment of H_D is incorrect (vide supra), then assignments of H_D and H_C must be switched which also requires switching the assignments of H_A and H_B. In fact, either assignment of the four-proton sequence results in identical patterns of exchange broadening for any given mechanism of chemical exchange (vide infra). In simulating DNMR spectra, chemical shifts will be assigned as shown in structure I of Scheme I.

Scheme I[a]



[a] Four possible rearrangement pathways for $[Cp_2Rh_2(Cot)]^{2+}$ and $[Cp^*_2Co_2(Cot)]^{2+}$: a, cw-1,2-M- and cw-1,2-M′-shifts; b, cw-1,3-M-shift; c, cw-1,3-M- and cw-1,3-M′-shifts; d, cw-1,2-M- and ccw-1,2-M′-shifts.

It is noteworthy that, in the intermediate exchange-broadened spectra of $[Cp_2Rh_2(Cot)]^{2+}$ at 258 and 270 K, the resonances at δ_C 5.10 and δ_D 4.57 are differentially broadened as compared to the other two Cot resonances. It is evident that the DNMR spectra of $[Cp_2Rh_2(Cot)]^{2+}$ may allow elucidation of the specific itinerary for conformational exchange in the complex.

III. Available Rearrangement Pathways in Transoid Bimetallic Complexes of Cot. In fluxional organometallic compounds of π-bonded polyolefins, the migration of the metal atom about the periphery of the conjugated system can occur via sequential 1,n-metal shifts.[6] The number "n" refers to the position of the carbon atom or the C–C bond to which the metal has moved relative to its original position. For fluxional mononuclear complexes of η^4- and η^6-bonded cyclooctatetraene, a specific 1,n-metal shift defines a unique rearrangement pathway which exchanges molecular conformers. In bimetallic complexes of the type $Cp_2M_2(\mu\text{-Cot})$, rearrangement pathways are inherently more complex. There are in principle four distinct 1,n-shifts (n = 2–5) available for each metal in these complexes. Since the polyolefin is flanked by two metal atoms, the rearrangement process could occur by unidirectional motions of both metals or movement of one metal in one direction combined with the movement of the other in the opposite direction. Such processes could involve identical 1,n-shifts or a combination of 1,n- and 1,m-shifts ($n \neq m$) for both metals. Interconversion of any two equivalent conformers could arise from different combinations of metal shifts above and below the Cot plane.

There are eight equivalent conformations of $[Cp_2Rh_2(C_8H_8)]^{2+}$ or $Cp^*_2Co_2(C_8H_8)]^{2+}$ which would result obviously from the fact that the two metal atoms have an equal probability of sharing any two adjacent carbon atoms around the Cot ring. A number of rearrangement pathways need to be considered. In Scheme I, we have summarized the results of various combinations of 1,2- and 1,3-metal shifts which are sufficient to interconvert equivalent conformations. The 1,4- and 1,5-shifts are not treated in Scheme I and will be addressed later. In Scheme I, the Cot ring is fixed in space while both metal atoms move around the ring. The structures are shown as if they are viewed from the top of one cyclopentadienyl plane. The Cp rings are not shown for the sake of clarity. The metal atoms above and below the Cot plane are represented by solid and open circles, respectively. The metal–carbon bonds above the plane of the Cot ring are represented by solid lines and those below the plane are represented by broken lines. The clockwise and counterclockwise shifts of the metal atoms above the plane are termed a *cw-1,n-M-shift* or a *ccw-1,n-M-shift*, whereas the same shifts below the Cot plane are termed a *cw-1,n-M′-shift* or a *ccw-1,n-M′-shift*, respectively.

At 245 K, only one spectrum is observed for $[Cp_2Rh_2(Cot)]^{2+}$. Multiple subspectra that might reveal diastereomeric conformations are not present. One spectrum at 245 K and the observed DNMR behavior is consistent with the presence of eight equivalent conformations of $[Cp_2Rh_2(Cot)]^{2+}$. Thus, we assume that the dirhodium dication is exchanging among eight equivalent conformations.

Assuming an initial conformation I for $[Cp_2Rh_2(Cot)]^{2+}$ (Scheme I), four additional equivalent conformations are structures II, III, IV, and V. Three other equivalent conformers are not shown. While equivalent structures I through V are related by symmetry, the transfers of magnetization among the Cot protons (i.e., the conformatiional exchange itinerary) from I to II, III, IV, and V are different. All four of the direct conversions of I to any one of the conformers II through V constitute different rearrangement mechanisms. A fifth rearrangement pathway is random exchange among all conformers. Having assigned the Cot proton chemical shifts (section II), DNMR stimulation models can be constructed which reflect the specific transfers of magnetization associated with each of the four interconversion itineraries in Scheme I as well as random exchange.[9] Utilizing a DNMR model involving exchange among eight singlets (eight Cot protons) and ignoring any scalar coupling, we computed the DNMR line shape for the five different itineraries at a first-order rate constant of 12 s^{-1} (parts a–e of Figure 2). For exchange-broadened spectra, ignoring the scalar coupling is a reasonable approximation due to the fact that the scalar coupling constants are much smaller than the frequency differences between any resonances.

The conversion of conformer I to II consists of cw-1,2-shifts of both metal atoms along pathway a in Scheme I. This process has the net effect of moving the C–C bond common to both metal atoms one bond clockwise. Couterclockwise 1,2-shifts of both metal atoms result in an equivalent transformation but with the common C–C bond shifted one bond couterclockwise. The magnetization transfers among protons associated with both interconversions are identical. For exchange between conformers I and II, it is evident from Scheme I that magnetization at δ_A 7.46 is involved in four exchanges with frequencies different from δ_A 7.46 (i.e., starting from I, $H_B \rightarrow H_A$, $H_A \rightarrow H_D$, $H_{A'} \rightarrow H_{B'}$, $H_{D'} \rightarrow H_{A'}$). An analogous situation is true for the magnetization at δ_B 5.98. In contrast, the magnetization of δ_C 5.10 is involved in only two processes which result in exchange with different frequencies ($H_C \rightarrow H_B$, $H_{B'} \rightarrow H_{C'}$) while another is degenerate ($H_{C'} \rightarrow H_C$). A similar situation prevails for the magnetization at δ_D 4.57. Therefore, for unidirectional 1,2-shifts of both metals, the resonances at δ_A 7.46 and δ_B 5.98 should broaden faster than those at δ_C 5.10 and δ_D 4.57, as illustrated in Figure 2a.

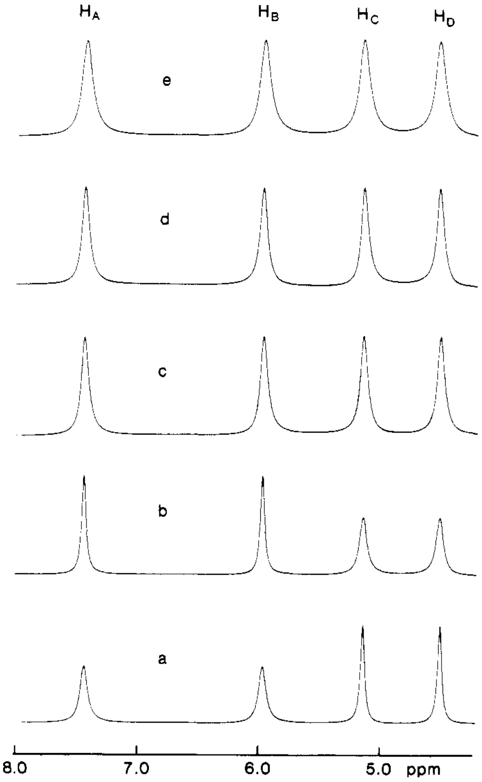


Figure 2. Theoretical spectra calculated for different exchange itineraries with a rate constant of 12 s^{-1}: (a) unidirectional 1,2-shifts of *both* metals, e.g., I to II (Scheme I); (b) 1,3-shift of *one* metal, e.g., I to III (Scheme I); (c) unidirectional 1,3-shifts of *both* metals, e.g., I to IV (Scheme I); (d) 1,2-shifts of both metals in opposite directions, e.g., I to V (Scheme I); (e) random exchange.

Conversion of I to III (Scheme I) involves a *cw-1,3-M-shift* only (pathway b). This process moves the C–C bond common to both metals three bonds counterclockwise. An equivalent transformation results from a *ccw-1,3-M′-shift.* Both processes involve identical site exchanges among the Cot protons. From a perusal of Scheme I, it can be shown that chemical exchange via these itineraries will result in the resonances at δ_C 5.10 and δ_D 4.57 broadening faster than those at δ_A 7.46 and δ_V 5.98, as illustrated in Figure 2b.

Conversion of I to IV involves two simultaneous cw-1,3-shifts of *both* metals (pathway c). Two simultaneous ccw-1,3-shifts of *both* metals will produce an equivalent transformation. For these processes, all pertinent magnetization exchanges occur at equal rates (Scheme I), and consequently, all four resonances broaden at the same rate (Figure 2c). Conversion of I to V consists of a *cw-1,2-M-shift* and a *ccw-1,2-M′-shift* (pathway d). At a rate constant of 12 s^{-1}, all four peaks are broadened to essentially the same extent (Figure 2d). In addition, this process allows only two separate two-site exchanges (i.e., δ_A 7.46 with δ_B 5.98 and δ_C 5.10 with δ_D 4.57). It does not allow complete exchange of all four sites and leads to a two-line

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(11) Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, 1058.

(12) Cramer, R. *Inorg. Chem.* **1962**, *1*, 722.

(13) Frankiss, S. G. *J. Phys. Chem.* **1963**, *67*, 752.

spectrum at fast exchange. This is clearly inconsistent with the observed DNMR behavior. The spectrum in Figure 2e corresponds to a random exchange of all eight protons.

The structures II through V in Scheme I have been shown to result from either 1,2- or 1,3-metal shifts. It can be shown that the same conformational exchanges result from suitable combinations of 1,4- or 1,5-metal shifts of any one metal followed by clockwise or counterwise 1,*n*-shift ($n \geq 2$) of the second metal. However, for the bimetallic complexes under discussion, an initial 1,4- or 1,5-metal shift produces an intermediate which has a bonding configuration very different from I and is presumably unstable. We assume that 1,4- and 1,5-shifts do not occur.

$[Cp_2Rh_2(Cot)]^{2+}$. The differential line-broadening observed for the experimental spectra of $[Cp_2Rh_2(Cot)]^{2+}$ (Figure 1) in the intermediate exchange region (e.g., at 258 K, where the line shape is very sensitive to a small variation in temperature) compares very well with the calculated spectrum in Figure 2b. That is, a 1,3-shift occurs, along pathway *b* in Scheme I. Indeed by using this exchange itinerary and superimposing the Cp singlet, excellent fits of theoretical to experimental DNMR spectra were obtained over a wide temperature range (Figure 1).[9] Calculation of DNMR spectra for various mixtures of the 1,3-metal shift exchange and 5–30% of each of the other mechanisms establish that the 1,3-metal shift is the predominant mechanism of rearrangement in the dirhodium complex. No reasonable fit was obtained for less than 90% of the 1,3-shift mechanism. The 10% margin may be considered to be within experimental error. Thus, for $[Cp_2Rh_2(Cot)]^{2+}$, the preferred itinerary for interchanging any two equivalent conformations involves a 1,3-shift of *one* metal atom with a free energy of activation (ΔG^{*}) of 14.5 kcal/mol (320 K). 1,3-Metal shifts, though not quite as common as 1,2-metal shifts, occur in $(\eta^4\text{-}C_7H_8)Fe(CO)_3$,[14] $(\eta^6\text{-}C_8H_8)M(CO)_3$ (M = Cr and W),[10a,b] and some (η^3-dienyl)palladium[11] complexes.

$[Cp^*_2Co_2(Cot)]^{2+}$. The slow-exchange ^1H NMR spectrum of the dicobalt complex in CD_3NO_2 at 245 K shows four Cot resonances at δ_A 7.34, δ_B 5.29, δ_C 3.55, and δ_D 3.02 with an integrated intensity ratio of 1:1:1:1 (Figure 3). The coupling constants derived from a simple four-spin model are $J_{AB} = J_{AD} = 4.5$ Hz, $J_{BC} = 5.0$ Hz, $J_{AC} = J_{CD} = 0$ Hz, and $J_{BD} = 0.5$ Hz. Chemical shifts were assigned in a manner strictly analogous to the Cot protons of the dirhodium complex and are referred to CHD_2NO_2 at δ 4.05. The simulated spectrum at 245 K using the above coupling constants is shown as the bottom trace in Figure 3b.

The experimental spectra for $[Cp^*_2Co_2(Cot)]^{2+}$ at various temperatures are shown in Figure 3a. The singlet resonance at δ 4.05 is due to CHD_2NO_2. The line-broadening effect seen for the Cot resonance as the temperature is raised from 245 to 300 K is just the reverse of what has been observed for the dirhodium compound; i.e., the two signals at higher frequencies due to H_A (δ 7.34) and H_B (δ 5.29) broaden faster than the two signals at lower frequencies due to H_C and H_D. This differential broadening is computed for the exchange process between the conformers I and II (Scheme I) and corresponds to pathway a. Thus, the mechanism for exchanging any two equivalent conformations of the dicobalt complex consists of two simultaneous or sequential unidirectional 1,2-shifts of *both* metal atoms. As in the dirhodium case, no reasonable fit was obtained for less than 90% of the itinerary involving unidirectional 1,2-shifts of both metals. Theoretical DNMR spectra calculated for various temperatures based on this model, with superposition of the CHD_2NO_2 peak at δ 4.05, give excellent fits to the experimental spectra (Figure 3b). As with the case of the dirhodium complex, at higher temperature the signals broaden further and at 356 K, all four resonances coalesce to a singlet at δ 4.80. The ΔG^{*} value for the exchange process is 14.0 kcal/mol (325 K).

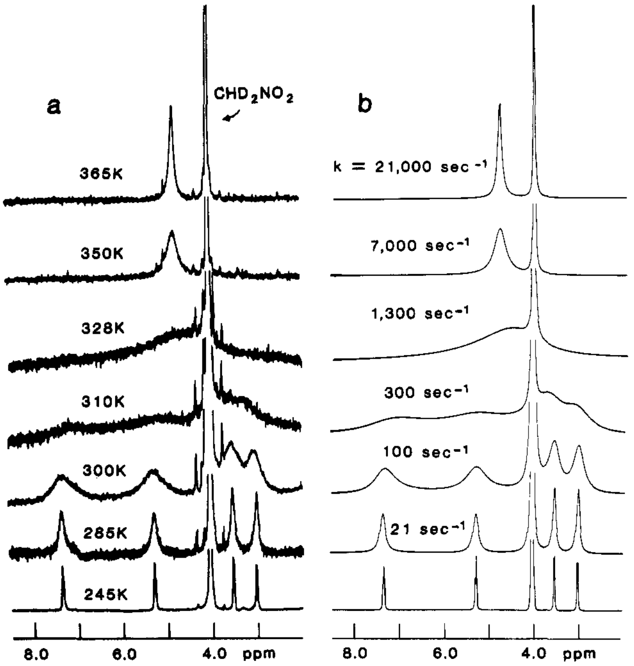

Figure 3. (a) Experimental Cot ^1H NMR spectra of $Cp^*_2Co_2(Cot)^{2+}$ and (b) calculated spectra based on unidirectional 1,2-shifts of both metals along pathway a in Scheme I.

The different rearrangement itineraries in $[Cp_2Rh_2(Cot)]^{2+}$ and $[Cp^*_2Co_2(Cot)]^{2+}$ may be attributed either to the nature of the metal atom or to the substituents on the cyclopentadienyl ring. Some insight would be found if the rearrangement pathway in either the non-methylated analogue of the dicobalt complex or the methylated analogue of the dirhodium complex could be determined. As mentioned earlier, the non-methylated dicationic cobalt complex was thermally too unstable to be isolated. Our own attempts to synthesize the permethylated analogue of the neutral dirhodium complex have not been successful.[16] As noted earlier, $[Cp_2Rh_2(Cot)]^{2+}$ and $[Cp^*_2Co_2(Cot)]^{2+}$ are the first examples of transoid bimetallic complexes with a bridging Cot ligand in which the mechanism of fluxionality has been elucidated. Two other fluxional complexes, $[Cp^*Co(Cot)RhCp^*]^{2+}$ and $Cp_2Ru_2(Cot)$, belonging to these slipped triple-decker species have been recently prepared,[5] but their rearrangement pathways are not yet known. Investigations of appropriate systems related to this class of compounds would be necessary to distinguish between the influence of the metal atoms and the substituents of the metal-bound ligands on the rearrangement mechanisms.

Finally, the question of the intervention of the true triple-decker structure 1 in these processes can be addressed. The dications $[Cp_2M_2(Cot)]^{2+}$ are 34-electron species and have the capability, at least from an electronic point of view,[1] of forming a completely delocalized triple-decker structure with a planar C_8H_8 ring being sandwiched by two CpM fragments lying along its C_8 axis.

This structure was considered as one of a number of possibilities in our original report of the two-electron oxidation of $Cp_2Co_2(Cot)$.[4a] Later these dications were shown

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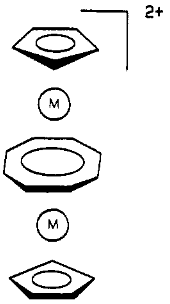
[14] (a) Mann, B. E. *J. Organomet. Chem.* **1977**, *141*, C33. (b) Karel, K. J.; Brookhart, M. *J. Am. Chem. Soc.* **1978**, *100*, 1619.



1, M = Co or Rh

to have a twisted Cot ring (vide supra).[4b] In addition, the observation at room temperature of substantial exchange broadening for the Cot protons NMR spectrum of $[Cp_2Rh_2(Cot)]^{2+}$ and a decoalesced albeit broadened spectrum of the Cot protons spectrum of $[Cp^*_2Co_2(Cot)]^{2+}$ clearly indicates chemical exchange among species that possess diastereotopic Cot protons. The decoalescence of the Cot protons spectra of both dications into four resonances at lower temperatures is consistent with C_2 molecular symmetry (vide supra) and inconsistent with the presence of a C_8 rotation axis. Indeed, our DNMR line-shape analyses (vide supra) rule out a random exchange pathway for conformational exchange which could involve a true triple-decker transition state with a C_8 axis. It may be that these later transition metals are simply too small to reside above the center of a planar eight-membered ring even in a transition-state structure. This leaves the only claim of a triple-decker having a planar Cot ring as $Ti_2(Cot)_3^{2-}$, for which the evidence is not strong.[15]

Experimental Section

NMR spectra were recorded on a Bruker WM-250 pulsed FT-NMR system. The samples were prepared in sealed NMR tubes under vacuum. Deuterated solvents were dried over activated molecular sieves (4Å) and degassed several times under vacuum before being distilled into the NMR tube. Temperature measurements are accurate within ±3 K. NMR line-shape simulations were carried out by using computer program DNMR4.[9]

Preparation of Compounds. All manipulations were done under nitrogen by using standard Schlenk tube techniques. The solvents were dried by standard procedures, and element analyses were done by Robertson Laboratory, Inc., Madison, NJ. The $Cp^*_2Co_2(Cot)$ was prepared according to literature.[8c] $Cp_2Rh_2(Cot)$ was prepared by a new method developed in our laboratory as described below. The same procedure has independently been developed by Salzer and co-workers.[5]

$Cp_2Rh_2(Cot)$.[8b] $[C_2H_4)_2RhCl]_2$[12] (195 mg, 0.5 mmol) was stirred with 280 mg (1.03 mmol) of CpRh(1,5-Cot) (Cp = cyclopentadienyl; Cot = cyclooctatetraene) in 10 mL of diethyl ether at room temperture for 48 h. An insoluble yellow precipitate formed gradually, displacing the red insoluble dimer. The precipitate was filtered out, washed several times with diethyl ether, and finally dried under vacuum to give 370 mg of $[CpRh(Cot)RhCl]_2$ as yellow cake which is virtually insoluble in common organic solvents. Its characterization is chiefly based on its chemical reaction with sodium cyclopentadienide, leading to the formation of $Cp_2Rh_2(Cot)$.

$$2CpRh(\eta^4\text{-}Cot) + [(C_2H_4)_2RhCl]_2 \rightarrow [CpRh(\mu\text{-}\eta^4,\eta'^4\text{-}Cot)RhCl]_2 + 4C_2H_4$$

$[CpRh(Cot)RhCl]_2$ (370 mg, 0.45 mmol) is reacted with 100 mg (1.14 mmol) of sodium cyclopentadienide in THF for about 1 h at room temperature. After removal of solvent under vacuum the residue was extracted with toluene (25 mL) and filtered through a fine frit. Removal of toluene gave 300 mg (0.68 mmol, 75%) $Cp_2Rh_2(Cot)$. For purification, it was recrystallized from toluene/pentane mixture and identified by its ^1H NMR spectrum.[8b]

$$[CpRh(\mu\text{-}\eta^4,\eta'^4\text{-}Cot)RhCl]_2 + 2\,NaCp \rightarrow 2Cp_2Rh_2(\mu\text{-}\eta^4,\eta'^4\text{-}Cot) + 2NaCl$$

$[Cp_2Rh_2(Cot)]^{2+}2ClO_4^-$. $Cp_2Rh_2(Cot)$ (100 mg, 0.23 mmol) was stirred with 104 mg (0.50 mmol) of silver perchlorate in 20 mL of diethyl ether for about 30 min at ambient temperature. The complex, precipitated as black crystalline material, was separated from the mother liquor and washed with small amounts of diethyl ether until free of silver ions. The residue was redissolved in 5 mL of nitromethane to form a deep red solution and was filtered quickly through a fine frit to remove the coprecipitated silver. After the solution volume was reduced to about 2 mL, the dication was crystallized by vapor diffusion of benzene into the solution. The red crystals were washed with small amounts of dichloromethane and dried under vacuum; yield 70 mg (48%). (Anal. Calcd C, 33.7; H, 3.04. Found: C, 33.83; H, 2.84.) [The hexafluorophosphate salt is obtained when $AgPF_6$ is employed as the oxidant.]

$[Cp^*_2Co_2(Cot)]^{2+}$ $2PF_6^-$. $Cp^*_2Co_2(Cot)$ (400 mg, 0.82 mmol) was dissolved in 50 mL of diethyl ether in a 100-mL flask. Silver hexafluorophosphate (500 mg, 2 mmol) was added, and the mixture was stirred for about 20 minutes at room temperature. A black precipitate separated was collected and washed several times with diethyl ether to remove the excess silver salt. It was then redissolved in 20 mL of acetone to give a dark red-brown solution and filtered through a fine frit to remove silver. Diethyl ether was added dropwise under stirring until precipitation started. When kept overnight at 253 K, the solution gave dark brown crystals of $Cp^*_2Co_2(Cot)^{2+}2PF_6^-$, yield 500 mg (78%). (Anal. Calcd: C, 42.98; H, 4.90. Found: C, 43.17; H, 4.91.)

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Registry No. $Cp_2Rh_2(Cot)$, 12295-91-9; $[Cp_2Rh_2(Cot)]^{2+}2ClO_4^-$, 113976-46-8; $[Cp^*_2Co_2(Cot)]^{2+}2PF6^-$, 113976-47-9; $[(C_2H_4)_2RhCl]_2$, 12081-16-2; CpRh(1,5-Cot), 55480-71-2; $[CpRh(Cot)RhCl]_2$, 104716-18-9; $[Cp_2Rh_2(Cot)]^{2+}2PF6^-$, 89958-69-0; $Cp^*_2Co_2(Cot)$, 81984-98-7; sodium cyclopentadienide, 4984-82-1.

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(15) Kolesnikov, S. P.; Dobson, J. E.; Skell, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 999.

(16) **Note added in proof**: This complex has recently been prepared by Dr. Albrecht Salzer at the University of Zürich.