coordinates involving the nontransferring hydrogens on C_2 and C_3. Two notable facts emerge.

Firstly, single-temperature k_H/k_D values are strongly model-dependent for given θ. The practice of equating a less than maximal k_H/k_D value with a specific value of $\theta^{6,10}$ is thus invalid. Secondly, all isotope effects are temperature-dependent to some extent, even for cases where θ is small. We have investigated in total more than 1000 TS models. *In not one case is a substantial primary k_H/k_D temperature-independent.*

The plot in Figure 1, based on 68 randomly chosen models, mostly with $\theta < 180°$, reveals that the magnitude of k_H/k_D at a given temperature is largely controlled by $[\Delta E_a]_D^H$, and not by A_H/A_D as alleged by Kwart.[3] It follows that only KIE's very close to 1.0 will have a negligible temperature dependence in the 0–100° range.

A more direct probe involved location of the TS on the MNDO potential energy surface and the calculation of the isotopic dependence of reactant and TS vibrational frequencies. The resultant KIE's are again decidedly temperature-dependent: $[\Delta E_a]_D^H = 1.09$ kcal mol^{-1}, $A_H/A_D = 1.06$. This is significant since the D···H···A TS angle is calculated to be 133.5°, which is in good agreement with the angle of 129.9° arising from ab initio calculations.[11] The MNDO KIE's are significantly lower than the experimental values,[5] but the latter are contaminated by secondary KIE's of unknown magnitude and may well be attended by hydron tunneling.

It is clear that the observed temperature-dependent KIE's for the sigmatropic rearrangement are not incompatible with a bent TS geometry. In the wider sense, the proposed criterion of TS geometry[3] appears to be without foundation. Some alternative explanations for the temperature-independent KIE's will be considered in the full paper.

Registry No. *cis*-1,3-Pentadiene, 1574-41-0; deuterium, 7782-39-0.

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Formation of Dinuclear Rhodium Dialkyl Complexes by Alkylation of a New Dinuclear Dianion and by Nucleophilic Addition of Alkyllithium Reagents across a Metal–Metal Double Bond

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We wish to report the products formed on one- and two-electron reduction of $[Cp*RhCO]_2^{1,2}$ $(Cp* = \eta^5\text{-}C_5Me_5)$ and the addition

(1) Nutton, A.; Maitlis, P. M. *J. Organomet. Chem.* **1979**, *166*, C21.

(2) $[Cp*RhCO]_2$ has a rich chemistry and has been utilized in the preparation of coordinately saturated dimers,[3] cluster compounds,[4] bridging carbene complexes,[4a,5] and dimetallacycles.[4s,6]

(3) Werner, H.; Klingert, B. *J. Organomet. Chem.* **1982**, *233*, 365.

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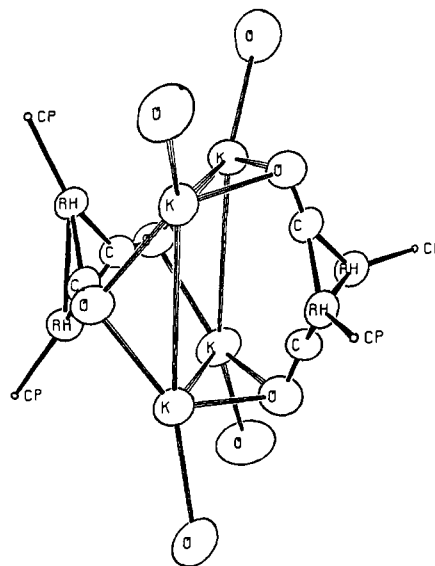
Figure 1. ORTEP diagram of $(K^+)_2[Cp*RhCO]_2^{2-}$·2THF showing the dimeric nature of the compound and its bonding scheme to the potassium ions (Cp* rings and the THF carbon atoms omitted for clarity). Bond distances (Å): Rh–Rh 2.606 (1) and 2.613 (1); K–K 4.205 (2), 4.040 (2), 4.162 (2), and 3.905 (3). Dihedral angles of Rh–Rh–(μ-CO) units are 122° and 125°.

of alkyllithium reagents across the formal rhodium–rhodium double bond in this molecule. To our knowledge the latter reaction is the first example of addition of an alkyllithium reagent across a metal–metal multiple bond. An X-ray diffraction study has been carried out on the potassium salt of the dianion obtained from the two-electron reduction; this complex shows a novel bonding scheme in which two dianion molecules are coordinated to a square of potassium atoms. The alkyl-substituted anions produced in the alkyllithium reactions react with organic electrophiles to provide a powerful new synthesis of dinuclear dialkyl complexes.

Treatment of neutral dimer $[Cp*RhCO]_2$ with Na/Hg or Na/K alloy in THF was carried out at room temperature using vacuum line techniques. The navy blue solution turned forest green after stirring for 0.5–1.5 h. Slow diffusion of pentane into this solution gave $K^+[Cp*RhCO]_2^-$. The potassium ion was also encapsulated with 2,2,2-cryptate[7] to form $[K(crypt)]^+$-$[Cp*RhCO]_2^-$. The IR spectrum of $[K(crypt)]^+[Cp*RhCO]_2^-$ in THF exhibited a single CO band at 1670 cm^{-1} (for comparison, neutral $[Cp*RhCO]_2$ shows a single CO band at 1736 cm^{-1} in THF; the corresponding cobalt radical anion exhibits a single CO band at 1690 cm^{-1}). The presence of a single band indicated a planar structure in solution for the $Rh_2(CO)_2$ unit similar to that observed for the isoelectronic cobalt system. ESR spectroscopy of the cryptate salt of the radical anion in 2-MeTHF showed a single broad line at room temperature ($\omega_{1/2} = 28$ G) with $g = 2.0704$. The lack of observed coupling to the ^{103}Rh ($I = {}^1/_2$) nuclei was not unusual due to the broadness of the line.[8] Cyclic voltammetric measurements showed the reduction of $[Cp*RhCO]_2$ to $[Cp*RhCO]_2^-$ was reversible and occurred at −1.15 V relative to a Ag/AgNO₃ couple.[9]

In the analogous cobalt series, attempts to form $[CpCo(CO)]_2^{2-}$ lead only to decomposition.[10]   In contrast, reduction of

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(7) Systematic name: 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane. Sold as Kryptofix 2,2,2 (obtained from Fluka).

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(9) CH₃CN solution, N(C₄H₉)₄⁺BF₄⁻ supporting electrolyte.

Scheme I

$R_a, R_b = CH_3, CH_2CH_3$

$Cp^* = Me_5Cp$
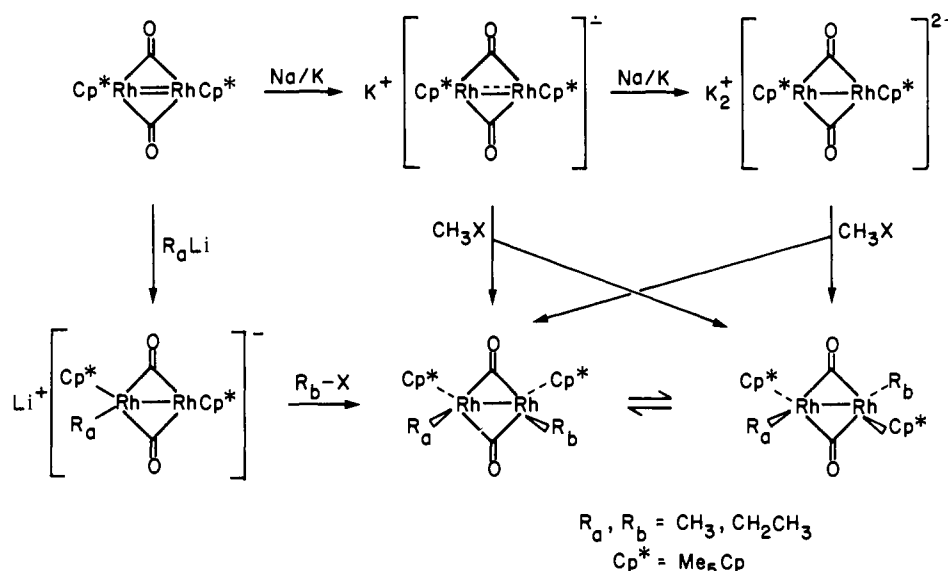
[Cp*RhCO]$_2$ with Na/K alloy in THF at room temperature for times longer than those required for single reduction proceeded with the initial navy solution turning forest green and then dark red. Slow diffusion of pentane into this solution led to the isolation of small, black, tabular crystals of the diamagnetic, 34-valence-electron complex (K$^+$)$_2$[Cp*RhCO]$_2{}^{2-}$ which were dried under high vacuum. The potassium atoms of this complex were also encapsulated with 2,2,2-cryptate to form [K(crypt)$^+$]$_2$-[Cp*RhCO]$_2{}^{2-}$. The IR spectrum of (K$^+$)$_2$[Cp*RhCO]$_2{}^{2-}$ in the CO region consisted of five moderately broad bands at 1747, 1690, 1669, 1635, and 1588 cm^{-1}. The IR of [K(crypt)$^+$]$_2$[Cp*RhCO]$_2{}^{2-}$ showed bands at 1694 and 1669 cm^{-1} and a weak band at 1743 cm^{-1}.

A crystal of the potassium salt of the dianion was isolated but not dried under vacuum. An X-ray crystallographic analysis[11] revealed an unusual structure with dianion molecules associated in pairs, joined by aggregates of four potassium atoms. Figure 1 shows how two dinuclear dianions are linked through their carbonyl oxygen atoms to an idealized square of potassium atoms; selected structural data are given in the figure caption. The coordination sphere of each potassium atom is completed by the oxygen of a THF molecule of solvation.

Reaction of either [Cp*RhCO]$_2{}^-$ or [Cp*RhCO]$_2{}^{2-}$ with CH$_2$Cl$_2$ in THF gave a mixture of the known bridging methylene complex [Cp*RhCO]$_2(\mu$-CH$_2)^{4a,5a,c}$ (10% yield) and neutral dimer [Cp*RhCO]$_2$ (10% yield). Reaction with 1,3-bis[p-tolyl-sulfonyloxy]propane gave the new rhodium dimetallacycle [Cp*RhCO]$_2$(CH$_2$)$_3$ (10% yield) and [Cp*RhCO]$_2$. Reaction with methyl iodide led to the cis and trans isomers of the dinuclear dimethyl complexes, [Cp*Rh(CO)(CH$_3$)]$_2$, in 3% total isolated yield, and [Cp*RhCO]$_2$.[12]

In the process of attempting to improve these yields, we recalled that phosphines have been observed to add unsymmetrically to metal–metal multiple bonds.[3,13] To explore an analogue of this reaction involving carbon nucleophiles, we treated neutral dimer [Cp*RhCO]$_2$ with methyllithium. Although we have not yet been able to isolate the product of this reaction, spectral data in THF-d_8 (^{1}H NMR δ 1.93, 1.74, –0.97; IR 1755 (m), 1710 (w), 1637 (s, br) cm^{-1}) are consistent with its formulation as the monoalkylated salt Li[Cp*$_2$Rh$_2$(CO)$_2$(CH$_3$)]. Treatment of this material with methyl iodide gives only *one* isomer (probably cis,[14] as shown in Scheme I) of [Cp*Rh(CO)(CH$_3$)]$_2$, in 59% isolated yield. In an analogous reaction, treatment of the initial methyllithium adduct with ethyl p-toluenesulfonate gives cleanly a single isomer of the *unsymmetrical* methyl, ethyl complex, uncontaminated by either the dimethyl or diethyl complexes, in 58% isolated yield. Finally, treatment of the neutral dinuclear dimer with ethyllithium followed by ethyl p-toluenesulfonate gives a single diethyl complex in 34% isolated yield. In each case, allowing the initially formed dialkyl complex to stand in benzene solution at room temperature slowly converts it into an equilibrium mixture of the cis and trans complexes, identical with those obtained by alkylation of the radical anion and dianion reduction products described above.

In summary, treatment of [Cp*RhCO]$_2$ with alkyllithium reagents followed by alkyl tosylates provides a route to dirhodium dialkyl complexes. This reaction appears to be general and proceeds in better overall yield and with higher stereospecificity than does alkylation of the corresponding radical anion and dianion. The properties of these dialkyl complexes—especially the time required for cis/trans isomerization—suggest that the metal–metal bonds are considerably stronger than those in the analogous cobalt complexes. The relationship of this characteristic to the chemistry of these materials is currently being explored.

Supplementary Material Available: Details of the synthesis of the compounds mentioned above, complete spectral and analytical data, X-ray experimental details, tables of positional parameters, general temperature factors, bond distances and angles, F_{obsd}, and F_{calcd}, and ORTEP diagram of other views of the molecule (73 pages). Ordering information is given on any current masthead page.

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(11) Crystal data: triclinic, P$\bar{1}$, a = 12.1653 (13) Å, b = 15.2618 (24) Å, c = 19.2691 (28) Å, α = 84.424 (12)°, β = 87.851 (11)°, γ = 77.837 (11)°, V = 3479.9 (12) Å^3, Z = 4; Mo Kα radiation, λ = 0.71073 Å; 9065 reflections, 6011 $F^2 > 3\sigma(F^2)$; corrected for decay, empirically corrected for absorption; R = 4.75%, R$_w$ = 7.66%.

(12) For the cobalt analogues of these complexes, see: (a) Theopold, K. H.; Bergman, R. G. Organometallics 1982, 1, 1571. (b) Theopold, K. H.; Bergman, R. G. J. Am. Chem. Soc. 1983, 105, 464. (c) Hersh, W. H.; Hollander, F. J.; Bergman, R. G. J. Am. Chem. Soc. 1983, 105, 5834. (d) Schore, N. E.; Ilenda, C. A.; White, M. A.; Bryndza, H. E.; Matturro, M. G.; Bergman, R. G. J. Am. Chem. Soc. 1984, 106, 7451.

(13) Hersh, W. H.; Bergman, R. G. J. Am. Chem. Soc. 1983, 105, 5846.

(14) On the basis of group theory considerations, the cis isomer of [Cp*Rh(CO)(CH$_3$)]$_2$ should have two IR stretches for the CO ligands but the trans isomer rigorously should have only one. Two IR stretches (1835 (w) and 1793 (s) cm^{-1}) are observed for the CO ligands in this molecule; on this basis we assign cis stereochemistry. We hope to do an X-ray diffraction study to confirm this assignment.