

Carbene Migration in a Cluster Complex. Observation of an Intermediate Containing a μ_3 -CH₂ Ligand

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The mobility of alkylidene ligands and other C₁ fragments on cluster complexes or metal surfaces is important in a number of catalytic processes such as the reductive oligomerization of CO (Fischer–Tropsch chemistry).¹ When present in a complex containing more than one metal atom, alkylidene ligands exhibit a marked preference for bridging (μ_2) coordination modes and are much less labile than CO ligands.² There have, however, been several reports of alkylidene migration in cluster complexes.³ The intermediates involved in alkylidene migration are generally so much higher in energy than ground-state structures that they have not been observed directly, and thus the mechanisms for migration are largely inferred from CO migration patterns and coordination modes. Recent theoretical⁴ and experimental studies have been interpreted as favoring terminal coordination modes for an alkylidene ligand in the intermediate linking two bridging coordination, ground-state structures in cluster complexes or on metal surfaces. Herein, we describe, for the first time, the direct observation of the intermediate involved in the migration of a methylidene ligand between two M–M edges in a cluster complex.⁵ ¹H and ¹³C NMR data suggest that the methylidene ligand in this species is best formulated as bridging all three metals. To our knowledge, this is also the first observation of a face bridging (μ_3) carbene ligand in a cluster complex involving d-transition metals.⁶

Recent work in our group has focused on the reactivity of a family of 46e⁻ trinuclear cluster complexes with the general formula, Cp^{*}M(CoCp)₂(CO)₂ (M = Co, Rh, and Ir).⁷ In the case of the RhCo₂-containing precursor, reaction with diazomethane gives the carbene complex Cp^{*}Rh(CpCo)₂(μ -CO)₂(μ -CH₂) (**1**).⁸ The crystal structure⁹ of **1** exhibits a triangular arrangement of metal atoms with the carbene ligand bridging a Rh–Co edge and the two carbonyl ligands bridging the remaining Rh–Co and Co–Co edges. The carbene and carbonyl ligands are all on one side of the M₃ plane in a “crown” arrangement. Spectroscopic data for **1** in solution at room temperature are consistent with this structure.⁹

The ¹³C NMR signal for the carbene ligand, observed at 138.3 ppm, is split into a doublet due to coupling to the rhodium atom ($J_{\text{Rh-C}} = 33$ Hz). Two carbonyl signals at 262.7 and 250.0 ppm ($J_{\text{Rh-C}} = 50$ Hz) are also observed, only one of which exhibits coupling to rhodium. The proton NMR signals for the methylene group are observed at 6.0 and 7.18 ppm. In contrast to previous reports for methylene ligands in trinuclear clusters, geminal coupling between the two methylene protons is very small ($^2J_{\text{HH}} \approx 0.5$ Hz). The two protons also exhibit different couplings to rhodium; the upfield signal exhibits a two bond coupling of 2.6 Hz, whereas the downfield signal exhibits only a 0.5 Hz coupling to rhodium. When **1** is left in solution at room temperature overnight, a second set of signals appears in the NMR spectrum which arises from the isomerization of the carbene ligand to the Co–Co edge and concomitant movement of the CO ligands to the Rh–Co edges (isomer **2**).⁹ At 330 K the rate of interconversion between **1** and **2** is $1.8 \times 10^{-4} \text{ s}^{-1}$ ($\Delta G^\ddagger = 104 \text{ kJ mol}^{-1}$) with an equilibrium constant of 2.62 at room temperature ($\Delta G^\circ(298) = -1.2 \text{ kJ mol}^{-1}$).

NOESY spectra of a mixture of **1** and **2** at 300 K¹⁰ exhibit strong *negative* NOE cross peaks between the two methylene proton signals of each isomer. With increasing temperature, the negative cross peak connecting the two methylene protons of **1** becomes weaker and above 360 K, a *positive* cross peak is observed, consistent with a dominant chemical exchange process between these two protons at this temperature (Figure 1A). The cross peak connecting the two protons of **2**, however, remains negative at all temperatures measured (Figure 1B). Quantitative analysis of the cross-peak intensities as a function of mixing time¹¹ gave a rate constant for the exchange process in **1** of 0.68 s^{-1} at 365 K corresponding to a free energy of activation of 91 kJ mol^{-1} .¹² Further NOESY experiments at 355 K yielded a positive cross peak between the two Cp ligand signals of **1**, indicating that the process interchanging the identities of the two methylene protons also interchanges the identities of two Cp–Co edges. The data above lead to the conclusion that the carbene ligand also moves between the two Rh–Co edges thus interchanging the two enantiomers of **1**.

An additional noteworthy feature in high-temperature NOESY spectra of **1** is the observation of a cross peak connecting both methylene protons to a very small signal at 8.45 ppm (Figure 1A). This signal exhibits coupling to rhodium ($J_{\text{Rh-H}} = 1.4$ Hz) and belongs to a species **3** which also exhibits single signals for the Cp and Cp^{*} ligand protons (C_s symmetry).¹³ Crystalline samples of **1** dissolved at low temperature do not contain species **3** initially. Upon warming to 300 K the signals for **3** are observed to grow into the NMR spectra. At equilibrium, this species occurs with a maximum abundance of ~1% relative to **1**. On the basis of these data, **3** is an intermediate in the interconversion of the two enantiomers of **1** where the methylene group moves directly from one Rh–Co edge to the other. To our knowledge, complex **3** is the first example of an observable intermediate involved in carbene migration in a metal cluster complex where the ground-state structures involve μ_2 -alkylidene ligands.

A parameter which distinguishes between the different coordination modes of an alkylidene ligand is the ¹³C NMR chemical shift. The normal chemical shift range for a terminal

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(6) Recently two examples of complexes containing μ_3 -methylidene groups bridging Al₃ and MA₂ (M = Zr, Hf) moieties have been described: Herzog, A.; Roesky, H. W.; Jäger, F.; Steiner, A.; Noltemeyer, M. *Organometallics* **1996**, *15*, 909.

(7) Barnes, C. E.; Dial, M. R.; Orvis, J. A.; Staley, D. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 1021.

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(9) Details concerning the crystal structure (**1**) and spectroscopic characterization for **1** and **2** may be found in the Supporting Information to this paper.

(10) Experiment conditions: ns = 32, $t_{\text{mix}} = 3$ s, 296 increments.

(11) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546. T_1 relaxation times and NOE enhancements between the geminal carbene protons were measured at temperatures where exchange is negligible and used to extrapolate the contribution of NOE to the cross peaks between the methylene protons at higher temperatures.

(12) Due to the decomposition of **1** at higher temperatures the temperature range within which such measurements can be performed is rather small (350–365 K); therefore, values for ΔH^\ddagger and ΔS^\ddagger are not reported.

(13) Spectral data for **3**: ¹H NMR (CD₂Cl₂) 8.3 (d, $J_{\text{Rh-H}} = 1.4$ Hz 2H), 4.57 (s 10H), 1.62 (d, $J_{\text{Rh-H}} = 0.6$ Hz 15H); ¹³C{¹H} NMR 145.3 ($J_{\text{Rh-C}} = 29$ Hz, $J_{\text{C-H}} = 145.3$ Hz), 89.7 (Cp), 10.6 (Cp^{*}-CH₃); IR (CD₂Cl₂) 1655 cm⁻¹.

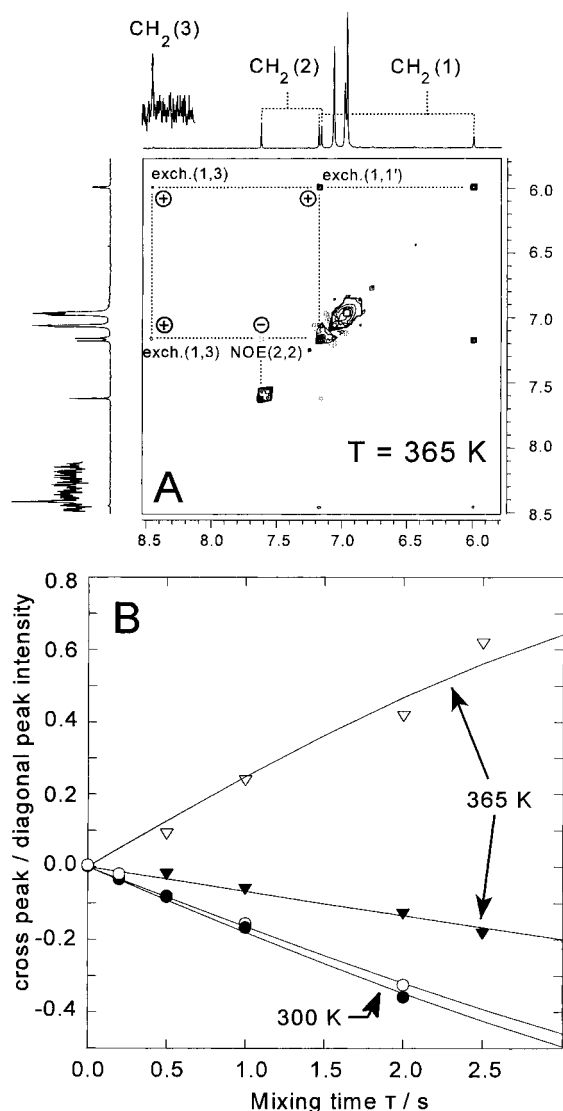


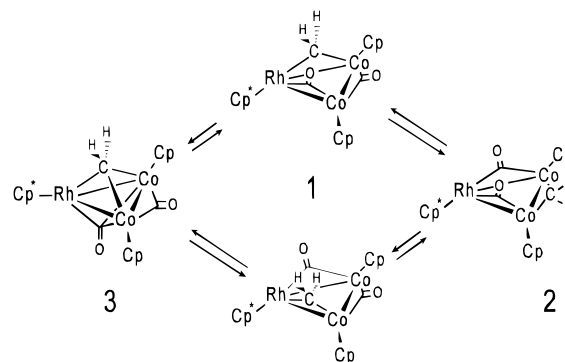
Figure 1. (A) Partial phase-sensitive NOESY spectrum (carbene region) of a mixture of isomers **1–3** in toluene- d_8 and (B) normalized cross-peak intensity vs mixing time for complexes **1** (open symbols) and **2** (filled symbols).

carbene ligand is 240 to 370 ppm, whereas bridging carbene ligands give rise to signals between 100 and 210 ppm.² A terminal carbene ligand coordinated to the rhodium atom in **3** should also exhibit a one-bond, C–Rh coupling constant about twice as large as is observed for a bridging coordination mode.¹⁴ By using a sample of **1** with the carbene ligand enriched (99%) in ^{13}C , an inverse detected, $^1\text{H}\{^{13}\text{C}\}$ correlation spectrum (HMQC pulse sequence)¹⁵ was obtained. In addition to the cross peaks due to the major isomers **1** and **2**, the spectrum exhibits a cross peak connecting the proton resonance of the carbene protons of **3** with a ^{13}C resonance at 145.3 ppm. Furthermore, the carbon–rhodium coupling constant ($^1J_{\text{Rh}-\text{C}}$) of 29 Hz is quite similar to that observed for **1**. These NMR data are not consistent with a terminal coordination mode for the carbene ligand in **3**.¹⁶ The simultaneous equilibration of CpCo vertices

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(15) (a) Müller, L. *J. Am. Chem. Soc.* **1979**, *101*, 4481. (b) Bax, A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Res.* **1983**, *55*, 301 (c) Bendal, M. R.; Pegg, D. T.; Doddrell, D. M.; *J. Magn. Res.* **1990**, *86*, 346. Experimental details may be found in the Supporting Information to this manuscript.

Scheme 1



with exchange of the methylene protons is not consistent with the carbene ligand remaining on any single edge M–M of the complex. We therefore propose that **3** contains a bridging carbene ligand. A geometry consistent with the above data is one in which the carbene assumes a μ_3 coordination geometry with the HCH plane parallel to the Co–Co edge. Although no ^{13}C NMR shifts have been reported for μ_3 -carbene ligands, by analogy with the trends observed for μ_2 - and μ_3 -carbonyl ligands,¹⁴ the observed chemical shift for the carbene ligand in **3** is quite reasonable for a μ_3 -bridging coordination mode.

Migration of the carbene ligand from one Rh–Co edge to the other also requires at least one CO ligand to move between Rh–Co edges. Several pathways can accomplish the required interchange. IR spectra of solutions of isomers **1–3** exhibit an extra band at 1655 cm^{-1} which is attributed to **3**. Such a CO stretching frequency is consistent with a triply bridging carbonyl ligand, presumably on the opposite side of metal plane from the carbene ligand in **3** as shown in Scheme 1.¹⁷ The carbonyl ligand bridging the Co–Co edge in **1** remains in place in **3**.¹⁸

The μ_3 coordination mode is well established for the carbene ligand and a few examples of μ_2 and μ_3 coordination modes for alkyl ligands are known in organometallic chemistry.¹⁹ It appears that intermediates involving μ_3 -alkylidene groups may be involved in the dynamics and reactions of transition metal cluster complexes and possibly on metal surfaces. The implications of these results with regard to carbene mobility and catalysis are being studied. The properties of these complexes and further examples of unusual bonding modes for carbene ligands are under investigation.

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Supporting Information Available: Listing of supporting characterization data for complexes **1** and **2** as well as X-ray data for **1**, including experimental procedures, tables of crystal data, atomic coordinates, thermal parameters bond lengths, angles, and ORTEP figures (11 pages). See any current masthead page for ordering and Internet access instructions.

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(16) Both the chemical shift of the methyldene protons and the C–H coupling constant for this group are also inconsistent with any type of agostic interactions involving this group and the metal atoms in the complex.

(17) NMR experiments with doubly labeled (>90% both in the carbene and CO ligands) show no C–C coupling between these ligands in **3** or any of the isomers studied here. This observation rules out possible ketenyl-type ligands in **3**.

(18) Attempts to elucidate the CO exchange pathways in these processes at the temperatures required (>55 °C) have been thwarted by quadrupole broadening due to cobalt even with ^{13}C -enriched samples.

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