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Methylidene and hydrazone complexes of the cluster family: $Cp'_3M_3(CO)_2(CH_2)$ ($M = Co, Rh, Ir$)

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Abstract

The reactions of diazoalkanes and trinuclear complexes of the form $Cp'M(CpCo)_2(CO)_2$ are described where Cp′ is one of several types of cyclopentadienyl ligands and M is either Co, Rh and Ir. Two types of products which preserve the trinuclear cluster skeleton are formed: the methylidene complex, reflecting loss of dinitrogen and incorporation of the methylidene ligand, and the hydrazone complex where incorporation of the intact diazoalkane occurs. NMR and X-ray structural investigations define the general and specific structural elements of these two product types. More detailed NMR investigations have been used to monitor the dynamic behavior of the methylidene ligand in these complexes. In several instances both degenerate and nondegenerate movement of this ligand in concert with the carbonyl ligands is observed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Methylidene complexes; Hydrazone complexes; Cluster family

1. Introduction

The properties and reactivity of metal complexes containing simple hydrocarbon fragments have occupied central positions in both the development and application of organometallic chemistry [1,2]. Two areas of recent interest are olefin polymerization and metathesis catalysts. In both reactions, it is now generally assumed that the critical intermediates in their catalytic cycles involve mononuclear alkyls or alkylidene complexes [3–5]. Although much less studied, polynuclear alkylidene complexes have also provided important insights into transition metal mediated catalysts involving polynuclear metal aggregates. For example, the reductive oligomerization of carbon monoxide (Fischer-Tropsche chemistry) is thought to involve several steps involving various C_1 fragments on metal surfaces [6,7]. Cluster complexes have long been proposed as possible models for such systems [8,9]. Although important differences between metal particles and cluster complexes are now recognized, many important insights into the properties of surface bound hydrocarbon ligands have accrued from solution studies of discrete cluster complexes [10].

An important question concerning the reactions of surface bound hydrocarbon fragments involves their ability to physically move from one coordination site to another, eventually encountering and reacting with other fragments on the surface. Alkylidene ligands favor μ_2-bridging coordination geometries in polynuclear complexes and on metal surfaces [11]. In the few cases where evidence for opening of the methylidene bridge has been collected, most mechanisms postulate the involvement of a terminal methylidene intermediate or transition state. Recently we described the first case in which an intermediate was observed in the movement of a methylidene ligand between the edges of the trinuclear cluster, $Cp^*Rh(CpCo)_2(CO)_2(CH_2)$ [12,13]. To our surprise, detailed NMR investigations into the identity of this intermediate lead to the conclusion that the methylidene ligand occupies a triply-bridging coordination geometry. Herein, we describe the synthesis and properties of several other members of this family of alkylidene complexes along with the hydrazone complexes formed when diazoalkanes react with unsatu-

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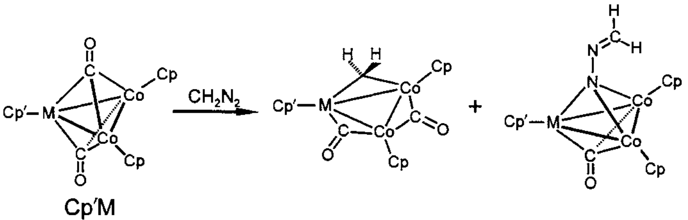
rated dicarbonyl cluster complexes of the general form $Cp'_3M_3(CO)_2$ (M = Co, Rh, Ir).

2. Results

The family of unsaturated 46e$^-$ cluster complexes of the form, $(Cp'M)_n(CpCo)_{3-n}(CO)_2$ (M = Co, Rh, Ir; $n = 1, 2$) readily react with electron donating ligands such as CO and acetylenes to form closed shell complexes [14,15]. Reaction of several members of this family with diazomethane and diazoethane yields either of two products as summarized in Eq. 1:



Cp'M		
CpCo	1	2
Cp*Co	-	3
Cp*Rh	4	5
Cp*Ir	6	-
Cp‡Co	-	7

(1)

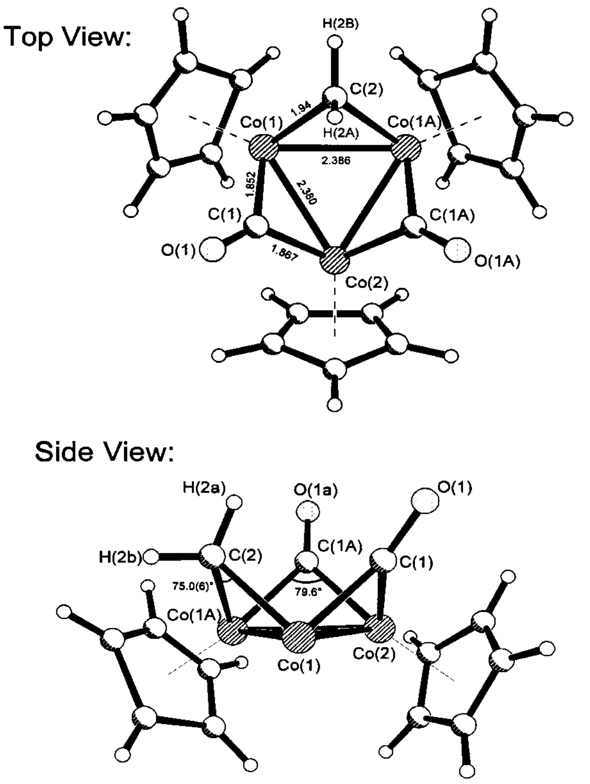


Fig. 1. Illustrations of the structure of **1** in the solid state. Note, in the side view, one Cp ring is not shown for clarity.

Table 1
Selected bond distances in **1**

Bond distance			
Co2–C1	1.867(14)	Co2–C1	1.867(14)
Co2–Co1	2.380(3)	C2–Co1a	2.380(3)
Co1–Co1a	2.386(4)	C2–Co1	1.94(2)
Co1–C1	1.852(15)	Co1–C2	1.94(2)
Bond angle			
Co1–Co2–Co1	60.16(11)	Co2–Co1–Co1	59.92(5)
Co1–C2–Co1a	75.9(7)	H2A–C2–H2B	113.1
O1–C1–Co1	143.1(15)	O1–C1–Co2	137.2(14)
Co1–C1–Co2	79.6(6)		

2.1. Reaction of $(CpCo)_3(\mu_3\text{-}CO)_2$ with diazomethane

The cluster complex $(CpCo)_3(CO)_2$ is the most reactive member in the family of 46e$^-$ dicarbonyl starting materials and spontaneously decomposes in solution [14,15]. Reaction of $(CpCo)_3(CO)_2$ with diazomethane was therefore performed by adding a solution of diazomethane directly to the solid compound instead of dissolving it beforehand in solvent. As products, both the methylidene and diazomethane adduct are obtained in about equal amounts. Chromatography of the mixture on silica gel separates these products with the less polar methylidene adduct eluting first (hexane:CH_2Cl_2) followed by the hydrazone complex (hexane:ether).

2.2. Methylidene adduct $(CpCo)_3(\mu\text{-}CO)_2(\mu_2\text{-}CH_2)$ (*1*)

Fig. 1 shows two views of the crystal structure of the methylidene adduct **1**, and Table 1 summarizes selected bond distances.

A crystallographically imposed plane of symmetry perpendicular to the metal ring bisects the complex in the solid state and includes the unique cobalt atom Co(2), the CH_2 group and one carbon atom of the Cp ring bound to Co(2). The methylidene and carbonyl ligands all bridge different Co–Co edges and are on the same side of the metal triangle similar to a number of tricarbonyl complexes such as $Cp^*Ir(CpCo)_2(\mu_2\text{-}CO)_3$ or $(CpRh)_3(\mu_2\text{-}CO)_3$ [16,17]. The Co–Co–Co angles observed for **1** are all close to 60° (60.2(1) and 59.92(5)°), while the carbonyl bridged edges are slightly shorter in length (2.379(3) Å) than the one bridged by the methylidene ligand (2.385(3) Å). These ligands are tilted out of the metal plane by an angle of 57.4° for the methylidene and 56.8° for the carbonyl ligands. The coordination about the methylidene carbon is a distorted tetrahedron with a reduced MCM angle of 75.0(6)°. One carbon–hydrogen bond points up, away from the metal triangle (H2a), while the other is directed outward horizontally away from the metal ring (H2b). The plane defined by the CH_2 moiety is perpen-

Table 2
Spectroscopic data for methylidene **1** and diazomethane **2** adducts of $(CpCo)_3(CO)_2$

	$(CpCo)_3(CO)_2(CH_2)$ (**1**)	$(CpCo)_3(CO)(NNCH_2)$ (**2**)
^{1}H-NMR	C_6D_6	C_6D_6
CH_2	7.63 d 1H, $^2J_{HH}\sim 1$ Hz,	7.95 d 1H, $J=13$ Hz
	6.62 d 1H, $^2J_{HH}\sim 1$ Hz,	7.08 d 1H, $J=13$ Hz,
Cp	4.536 s, 10H; 4.532 s, 5H	4.56 s, 15 H
^{13}C-NMR	CD_2Cl_2	C_6D_6
	253.86 (CO), 139.11 (t, CH_2)	141.53 (dd, $J_{CH}=163$ Hz, $J_{CH}=181$ Hz, CH_2)
	89.61 (Cp), 88.58 (Cp)	83.86 (Cp)
IR (KBr)	1814, 1766;	1667
MS (EI)	442 (1%, M^+);	442 (100%, M^+);
	414 (35%, M^+-CO);	414 (6%, M^+-CO);
	384 (32%, M^+-CO, H_2CO);	387 (24%, M^+-CO, HCN);
	189 (100%, $[Cp_2Co^+]$)	321 (100%, M^+-CO, HCN, CpH)
		HRMS: $M^+=441.93261$ (calc. 441.9337)

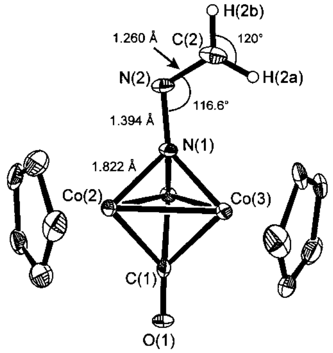


Fig. 2. ORTEP illustration of the structure of **2** in the solid state. Note, one Cp ring is not shown for clarity.

dicular to the plane for the two methylidene carbon–cobalt bonds as well as to the metal triangle and lies in the plane of symmetry bisecting the molecule. The centroids of the Cp ligands are found below the metal plane by angles of 32.7 and 25.8° towards the opposite face of the cluster resulting in an angles of 57.3° and 64.2° between the Cp ring planes and the plane of the metal triangle.

The ^{1}H-NMR spectrum of **1** exhibits two signals for the protons of the Cp ligands with a relative intensity of 2:1. This is consistent with a static structure in which the methylidene ligand is bridging one cobalt–cobalt edge causing two of the three CpCo vertices to be equivalent. Furthermore, two signals at 7.63 and 6.62 ppm are observed for the two diastereotopic methylene hydrogens of the methylidene ligand as expected for a rigid group bridging one Co–Co bond. A NOESY spectrum ($T=300$ K, $T_{mix}=2$ s) exhibits a strong negative cross peak connecting the methylene protons. The upfield methylene signal at 6.72 ppm displays an additional crosspeak with the signal for the two equivalent Cp rings, consistent with its assignment as the signal associated with the hydrogen closest to the metal plane (H2b). The downfield signal is assigned to the hydrogen pointing up (H2a). Another interesting feature of the ^{1}H-NMR spectrum is the fact that the geminal coupling constant $^2J_{HH}$ between the two methylene protons is approximately 1 Hz. This is in contrast to similar carbonyl based trinuclear methylidene complexes where a geminal coupling constants of around 5 Hz have been reported [18,19].

The ^{13}C-NMR spectrum for **1** is consistent with the conclusions drawn from the ^{1}H-NMR spectrum. Two signals are observed in the Cp region and the signal of the methylidene carbon at 139.1 ppm is consistent with an edge bridging coordination geometry [11]. A proton coupled ^{13}C-NMR spectrum revealed that this signal is split into a triplet ($^1J_{CH}\approx 136$–140 Hz) indicating equal or very similar coupling constants to the two diastereotopic protons of the CH_2 group. A signal at 253.9 ppm is observed for the two equivalent carbonyl carbons bridging the remaining Co–Co edges. The resonances for both the methylidene and carbonyl carbons are significantly broadened by scalar coupling to the Co nuclei [20] thereby prohibiting more accurate determination of the C-H coupling constants.

The IR spectrum (KBr) for **1** shows two carbonyl stretches at 1814 and 1766 cm^{-1} supporting the presence of edge bridging carbonyl ligands. The mass spectrum exhibits a very weak molecular ion peak at $m/q=442$, but a strong peak for M^+–CO indicating facile loss of CO. No peak due to loss of two CO ligands is observed ($m/q=386$), although a fragment peak consistent with loss of one CO plus loss of H_2CO is observed ($m/q=384$). The most intense fragment peak seen in the mass spectrum is consistent with the cobaltocenium cation Cp_2Co^+ ($m/q=189$). A summary of all NMR, IR and MS data for **1** is given in Table 2.

2.3. Diazomethane adduct $(CpCo)_3(\mu_3\text{-}CO)(\mu_3\text{-}NNCH_2)$ (2)

Single crystals of $(CpCo)_3(\mu_3\text{-}CO)(\mu_3\text{-}NNCH_2)$ (**2**) suitable for x-ray diffraction were obtained by recrystallization from methylene chloride/hexane at −20°C. A side view of the crystal structure is shown in Fig. 2, and selected bond distances and angles are listed in Table 3.

The three Co atoms are arranged in a triangle in which the Co–Co–Co angles are all equal to 60° within one degree. The diazoalkane coordinates to one face of the metal triangle via its terminal nitrogen atom and the μ_3-carbonyl ligand is found on the opposite face. The carbon–nitrogen bond distance is 1.260(6) Å, significantly shorter than that found in CH_2N_2 (1.34 Å) [21] and consistent with a C=N double bond (average for C=N 1.28 Å [22,23]). The nitrogen–nitrogen bond distance of 1.394(5) Å, on the other hand, is significantly longer than in free CH_2N_2 (1.12 Å) [21] and resembles a N–N single bond (1.43 Å in $H_2N_2O_2$) rather than a N=N double bond (1.21 Å in N_2F_2) [24]. The angle N(1)–N(2)–C(2) is 116.9(4)°, compared with 180° in CH_2N_2, suggesting sp^2 hybridization for N(2). Such an angle indicates that coordinated diazomethane in **2** is best described as a $4e^-$, μ_3-hydrazone ligand. As a result, the CH_2 group is bent towards one CpCo corner with one hydrogen pointing up and the other pointing down.

Table 3
Selected bond distances (Å) and angles (°) fot the diazomethane complex

Bond distances			
Co(1)–N(1)	1.821(3)	Co(1)–C(1)	1.970(5)
Co(1)–Co(3)	2.3879(8)	Co(1)–Co(2)	2.3900(9)
Co(2)–N(1)	1.822(3)	Co(2)–C(1)	1.942(4)
Co(2)–Co(3)	2.4218(8)	Co(3)–N(1)	1.832(4)
Co(3)–C(1)	1.979(4)	C(1)–O(1)	1.189(5)
C(2)–N(2)	1.260(6)	N(1)–N(2)	1.394(5)
Bond angles			
Co(3)–Co(1)–Co(2)	60.91(3)	Co(1)–Co(2)–Co(3)	59.50(2)
Co(1)–Co(3)–Co(2)	59.59(2)	O(1)–C(1)–Co(2)	136.4(3)
O(1)–C(1)–Co(2)	133.9(3)	O(1) = C(1)–Co(3)	135.0(3)
N(2)–N(1)–Co(1)	127.2(3)	N(2)–N(1)–Co(2)	126.8(3)
N(2)–N(1)–Co(3)	137.2(3)	C(2)–N(2)–N(1)	116.9(4)

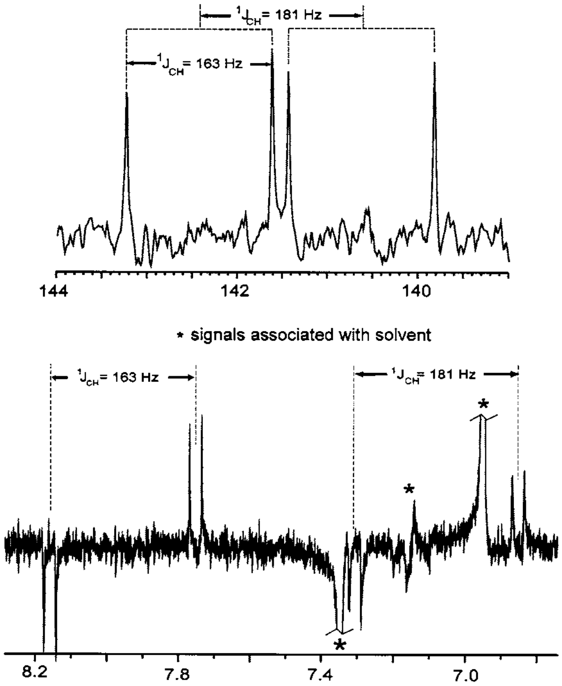


Fig. 3. Top: proton coupled ^{13}C-NMR signals for the terminal methylene group of the hydrazone ligand. Bottom: ^{13}C satellite signals of the methylene proton resonances. Signals appear as antiphase doublets due to the different $^1J_{CH}$ coupling constants.

Table 2 summarizes the spectroscopic data found for the diazomethane adduct **2**. The room temperature proton NMR spectrum exhibits only one signal for the Cp hydrogens indicating that all three CpCo edges are equivalent. Such an equivalency can be explained by fast rotation of the N=CH_2 moiety about the N–N bond in solution, consistent with a single bond as suggested by the crystal structure data. Two signals are observed for the methylene hydrogens indicating that there is no fast rotation about the C=N bond as expected for a double bond. The spectroscopic data therefore also support the designation of the coordinated diazomethane as a hydrazone ligand. The chemical shifts of the methylene protons of the hydrazone ligand are in the same region as those observed for the methylidene ligand in **1**. In contrast to the methylidene ligand, however, a large geminal coupling is observed between the two hydrazone protons ($^2J_{HH} = 13$ Hz).

In agreement with the ^1H-NMR spectrum, the ^{13}C-NMR spectrum exhibits only one signal for the Cp ring carbons, and a signal for the terminal methylene group of the CH_2N_2 ligand at 141.53 ppm. We were not able to observe a signal for the carbonyl carbon which would be expected at 250–270 ppm.

An interesting spectroscopic feature this complex is revealed by the proton coupled ^{13}C-NMR spectrum. As shown on top of Fig. 3, a doublet of doublets is observed instead of the triplet found for the methylidene adduct **1**.

This indicates that the two diastereotopic methylene protons have different coupling constants $^1J_{CH}$ to the methylene carbon (163 and 181 Hz). In order to assign the coupling constants to the two methylene proton signals, the ^{13}C satellites in the proton spectrum were recorded. These appear as doublets with 0.55% intensity of the main proton signal. In order to distinguish these signals from impurities or spinning sidebands, a pulse sequence employing a double quantum filter was applied which suppresses all signals arising from protons not bound to ^{13}C [25]. Such an experiment yields the spectrum shown in the bottom of Fig. 3 where the ^{13}C satellite peaks appear as antiphase doublets. One can see that the downfield proton exhibits the smaller coupling constant of 163 Hz, whereas the larger coupling of 181 Hz can be assigned to the upfield proton signal.

The difference in $^1J_{CH}$ coupling constants is caused by the proximity of these protons to the lone pair

Table 4
Spectroscopic data of the methylidene **6** and hydrazone adducts **3**, **5**, and **7**

	Methylidene	Hydrazone		
L–M	Cp*Ir (**6**) [a]	Cp*Co (**3**)	Cp*Rh (**5**)	Cp‡Co (**7**)
^1H-NMR (ppm)	C_6D_6	C_6D_6	C_6D_6	C_6D_6
CH_2	7.36 d $^2J = 1$Hz 6.05 d $^2J = 1$ Hz	7.91 d $^2J = 13.7$ Hz 7.23 d $^2J = 13.7$ Hz	7.57 d $^2J = 13.8$ Hz 7.12 d	7.80 d $^2J = 13.5$Hz 7.14 d $^2J = 13.5$ Hz
Cp	4.59, 4.55	4.48 (10H)	4.56 s (10H)	4.481 (10H)
Cp*	1.70 (15H)	1.56 (15H)	1.61 s (15H)	1.89, 1.43
^{13}C-NMR (ppm)	CD_2Cl_2	C_6D_6	C_6D_6	C_6D_6
CO	268.3, 234.4	276.7	Not observed	273.3
CH_2	112.9 d	139.4 dd $^1J_{CH} = 162$ Hz $^1J_{CH} = 180$ Hz	139.9 dd $^1J_{CH} = 162$ Hz $^1J_{CH} = 180$ Hz	140.6 dd $^1J_{CH} = 163$ Hz $^1J_{CH} = 181$ Hz
Cp	88.8, 88.3	83.1 (d)	83.2 (d)	83.69 d
Cp*‡	98.6, 9.7	92.8(s), 9.5(q)	97 (s), 9.95 (q)	127.3, $^1J_{CF} = 270$ Hz; 95.5; 94.1; 9.46; 8.98, $^4J_{CF} = 2$ Hz
IR (cm^{-1}) ν_{CO}	KBr: 1782, 1752, 1743	KBr: 1670	KBr: 1657, 1680	
MS (m/e)	646 (3, M^+) 618 (58, −CO) 590(100, −2CO) HRMS: 590.0383 (exp) 590.0406 (cal)	512 (100, M^+); 484 (8, −CO); 457 (22, −CO, −HCN); 391 (72, −CO, −HCN, −CpH); 259 (41, $[Cp^*CoCp]^+$) 189(19, Cp_2Co^+)	556 (100, M^+); 528 (3, −CO); 500 (20, −CO, $-N_2$); 435 (88, −CO, −HCN, −CpH); 303 (81, $[Cp^*RhCp]^+$) EA: found(calc.) C: 47.01(45.9) H: 4.88(4.78) N: 5.04(4.83)	566 (100, M^+) 538 (11, −CO) 510 (7, −CO, $-N_2$) 414 (31, −CO, −CpCo); (13, $[Cp^‡CoCp]^+$) HRMS: 565.981 (exp.) 565.984 (calc.)

[a] Ref. [16].

electrons on N(2). In compounds containing a –N=CHR group, a proton *cis* to the nitrogen lone pair experiences a larger ^{13}C–^1H coupling than a proton *trans* to the lone pair of the nitrogen [26,27]. Aldoxime ($H(CH_3)C{=}N{-}OH$), for example, shows a C–H coupling of 163 Hz for the *E*-isomer where the hydrogen is *trans* to the lone pair and 177 Hz for the *Z*-isomer with the hydrogen *cis* to the lone pair. Similar effects have been observed in azirines. In the case of the $(CpCo)_3(\mu_3\text{-}CO)(\mu_3\text{-}NNCH_2)$ the proton pointing up and away from the Co_3 triangle is *cis* to the nitrogen lone pair and is expected to show the larger C–H spin-spin coupling whereas the hydrogen pointing down should exhibit the smaller coupling. One can therefore assign the downfield signal at 7.95 ppm ($J_{CH} = 163$ Hz) to the C–H bond pointing down (H2a) and the upfield signal at 7.08 ppm ($J_{CH} = 181$ Hz) to the hydrogen pointing up (H2b). These findings are also supported by NOE measurements; upon irradiation of the Cp proton resonance, the proton signal at 7.95 ppm exhibited twice the NOE as the signal at 7.08 ppm consistent with the above conclusions.

The IR spectrum of **2** exhibits one band for the CO stretching vibration at 1667 cm^{-1} consistent with one face bridging carbonyl ligand. The MS shows a strong parent ion peak relative to the fragment peak due to loss of one CO ligand (90:5) indicating that loss of CO is less facile than in the corresponding methylidene complex. Furthermore, a fragment peak due to the combined loss of CO and HCN is observed. It should be noted that the nominal mass of the parent ion of the hydrazone complex is the same as that for the methylidene complex **1**. A high resolution MS (Table 2) and elemental analysis, however, confirm the presence of the hydrazone ligand in the structure of **2**.

2.4. Reaction of the heteronuclear complexes $Cp^*M(CpCo)_2(\mu_3\text{-}CO)_2$ (M = Co, Rh, Ir) $Cp^‡Co(CpCo)_2(\mu_3\text{-}CO)_2$ with diazomethane

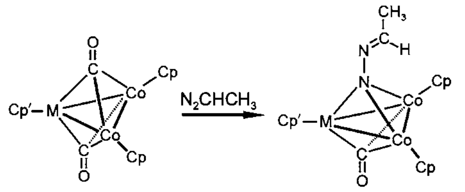
The products obtained from the reaction of the heteronuclear cluster complexes $Cp^*M(CpCo)_2(\mu_3\text{-}CO)_2$, (M = Co, Rh, Ir) appear to depend mainly on the identity of the metal M. In the case of M = Co only the hydrazone adduct **3** is observed in significant amounts, whereas for M = Ir, only methylidene adduct **6** is isolated. M = Rh yields a mixture of the methylidene adduct **4** [12] and the hydrazone adduct **5**. Reaction of the complex Cp‡Co(CpCo)$_2$(CO)$_2$ (Cp‡: tetramethyl trifluoromethylcyclopentadienyl ligand) [28] yields only the corresponding hydrazone complex **7**. Spectroscopic and MS data for these complexes are summarized in Table 4.

The ^{1}H-NMR spectrum of the Ir methylidene complex **6** closely resembles that observed for the corresponding cobalt and rhodium complexes **1** and **4** [12]. All of these methylidene complexes exhibit two signals for the hydrogens of the Cp ligands indicating that the methylidene ligand bridges the Cp*M–CpCo edge resulting in two inequivalent CpCo edges. No evidence for the isomer in which methylidene ligand bridges the Co–Co edge is found for the crude products in these reactions.

The hydrazone adducts **3**, **5**, and **7** also exhibit spectra very similar to the that observed for (CpCo)$_3$(μ_3-CO)(μ_3-NNCH$_2$) (Table 4). Only one signal is observed for the protons of the Cp ligands in all cases.

2.5. Reaction with diazoethane

Reaction of the unsaturated trinuclear complexes with diazoethane yields exclusively the hydrazone adducts **8**–**10**.



Cp'M	
CpCo	8
Cp*Rh	9
Cp*Ir	10

In the case of Cp*Ir(CpCo)$_2$(μ_3-CO)$_2$(μ_3-NNCHMe) (**10**) the product appears to be very unstable and decomposes to unknown products when purification by low temperature chromatography is attempted. The methylene carbons in both **8** and **9** exhibit a carbon-proton coupling constant of $^1J_{CH} = 160$ Hz indicating that the hydrogen is *trans* to the lone pair on the nitrogen and pointing downwards towards the metal cluster. Accordingly, the methyl group should be directed up and away from the metal triangle. These observations are consistent with the crystal structure reported for the Cp*Co analog [29]. A summary of the spectroscopic and MS data for all diazoethane complexes is shown in Table 5.

Table 5
Spectroscopic data of diazoethane adducts LM(CpCo)$_2$(μ_3-CO)(μ_3-NNCHMe)

LM	CpCo (**8**)	Cp*Rh (**9**)	Cp*Ir (**10**)
^{1}H-NMR	(C$_6$D$_6$)	(CD$_2$Cl$_2$)	(C$_6$D$_6$)
C*H*Me,	8.46 (q)	8.26 (q)	8.07 (q)
CHC*H*$_3$	1.81 (d)	2.18 (d) $^3J_{HH} = 5.6$ Hz	1.73 (d)
	$^3J_{HH} = 5.5$ Hz		
Cp	4.60	4.53	4.44
Cp*	–	1.715	1.85
^{13}C-NMR	CD$_2$Cl$_2$:	CD$_2$Cl$_2$:	
*C*O	277.6	273	
*C*HMe	153.7 dd	154.5 dq	
CH*C*H$_3$	$^1J_{CH} = 160.5$ Hz	$^1J_{CH} = 160$ Hz	
Cp	$^2J_{CH} = 7.3$ Hz	$^2J_{CH} = 7$ Hz	
Cp*	19.3 qd	20.7 qd	
	$^1J_{CH} = 127.9$ Hz	$^1J_{CH} = 127.7$ Hz	
	$^2J_{CH} = 11.0$ Hz	$^2J_{CH} = 11$ Hz	
	84.1 s	85.1 (d)	
	–	99.4 (s), 12.0 (q)	
IR	(KBr): 1697 cm^{-1}	(Hexane): 1682 cm^{-1}	
MS	456 (88%, M$^+$)	567 (100%, M$^+$)	
	428 (5%, −CO)	542 (8%, −CO)	
	387 (22%, −CO, −MeCN)	435 (90%, −CO, −MeCN, −Cp−H)	
	321 (100%, −CO, −MeCN, −CpH)	303 (80%, [Cp*RhCp]$^+$)	
	189 (85%, Cp$_2$Co$^{\bullet +}$)	HRMS:	
		569.998(exp.)	
		570.000(calc.)	

Table 6
Free energies of activation ($\Delta G^{\ddagger}$) for methylidene migration in **1**, **4**, **6**. Values are given in k*J* mol^{-1}

Process	CpCo (**1**)	Cp*Rh (**4**) [a]	Cp*Ir (**6**)
MCo → MCo	86.5 [d]	96.0 [b], 92.1 [c]	99.9 [b]
MCo → CoCo	–	104.7 [b], 104.0[c]	–

[a] Ref. [12].
[b] 298 K.
[c] 360 K.
[d] 350 K.

*2.6. Methylidene fluxionality in cluster complexes $Cp^*M(CpCo)_2(CO)_2(CH_2)$ (M = Co, **1**; Rh, **4**; and Ir, **6**)*

Based on the observation of a large ion signal for loss of CO from the parent ions of the methylidene complexes, we investigated the thermal stabilities of the members of this family of cluster methylidene complexes. The iridium complex **6** reversibly loses one CO ligand and forms the carbyne hydride complex $Cp^*Ir(CpCo)_2(\mu_3\text{-}CO)(\mu_3\text{-}CH)(\mu\text{-}H)$ [30]. The analogous Co and Rh methylidene complexes **1** and **4**, decompose in solution at temperatures considerably lower than found for **6**. Unfortunately, several species are formed and so far no stable, purified products have been isolated in either case. NMR spectra collected at room temperature do not show the characteristic signals indicating the presence of carbyne or hydride ligands in the products. Low temperature NMR spectra of the decomposition product of the Rh methylidene complex **4** revealed one signal at 15 ppm and several signals in the hydride region between −20 and −25 ppm. It is therefore possible that a Cp*Rh containing carbyne hydride complex is formed in this case. However, the pattern of signals decoalescing at low temperature is too complex to be caused just by a single complex. Further investigations are needed to establish the nature of these products.

A detailed account of the fluxionality of the methylidene and carbonyl ligands in **4** has already appeared [12]. Evidence for methylidene fluxionality has also been observed in the cobalt (**1**), and iridium (**6**), complexes. In the case of the all-cobalt complex **1**, movement of the methylidene ligand between different Co–Co edges is degenerate. In the Ir–Co methylidene complex (**6**), evidence for exchange of the methylidene ligand between the two Ir–Co edges is observed while evidence for the isomer having the methylidene ligand bridging the Co–Co edge has not been observed. As in the case of **4**, exchange between the two diasteriotopic protons of the bridging methylidene ligand indicates movement of this ligand in complexes **1** and **4**. The temperature dependencies of phase sensitive NOESY experiments were investigated, focusing on the cross peaks relating the diasteriotopic proton signals of the bridging methylene groups in methylidene complexes **1** and **6**. After separating out NOE contributions to cross peak intensity [25], exchange rate constants are obtained. Free energies of activation ($\Delta G^{\ddagger}$) for methylidene migration between the M–Co edges takes place in both adducts at a rate comparable to the one found in **4**. Table 6 summarizes the activation barriers found for methylidene migration in complexes **1**, **4** and **6**.

3. Discussion

The reaction of the unsaturated cluster complexes of the general form $(Cp'M)_n(CpCo)_{3-n}(CO)_2$ with diazoalkanes at low temperature leads to both methylidene and hydrazone adducts. The μ_3-hydrazone complexes do not appear to be precursors to the alkylidene complexes due to their high thermal stability and thus two separate reaction manifolds must be accessible to the intermediates formed in the intial steps of the reaction.

In the case of the heteronuclear complexes $Cp^*M(CpCo)_2(CO)_2$, the tendency to form the methylidene product depends on the nature of the metal and increases in the order Co < Rh < Ir. The Ir complex forms only the methylidene adduct, whereas the Co complex forms only a hydrazone adduct. The Rh complex takes an intermediate position between these two extremes, forming both methylidene and hydrazone adducts. This trend might be correlated to the increase in π-backbonding capability from Co to Ir. An important contribution to the bonding of a bridging methylidene ligand involves backbonding from occupied metal–metal σ-antibonding MOs into the empty p_{π}-orbital of the methylidene ligand [11,31]. A similar situation should exist for the frontier orbitals of the corresponding trinuclear framework M_3L_9 [32]. The hydrazone ligand, on the other hand, is not a π-acceptor. It is conceivable that increased backbonding in the product thermodynamically stabilizes a methylidene ligand over a hydrazone ligand. Furthermore, increased π-backbonding of the metal also makes loss of CO more difficult, thus possibly introducing a higher kinetic barrier to the formation of hydrazone complexes.

The products from the diazoalkane reaction with the series $(Cp'Co)(CpCo)_2(CO)_2$ (Cp′ = Cp, Cp*, Cp‡) indicate that steric factors also influence the course of the reaction. Both the complexes with the sterically demanding pentasubstituted cyclopentadiene ligands (Cp* and Cp‡) form only hydrazone adducts. On the other hand, the all-CpCo containing cluster complex forms both methylidene and hydrazone adducts in comparable amounts. Although not described in detail here, we have briefly investigated the reactions of other diazoalkanes bearing different substituents (e.g. dimethyl, phenyl, diphenyldiazomethane) with the unsaturated cluster starting materials. In all cases only hydrazone products were obtained.

In the case of the heteronuclear methylidene complexes $Cp^{*}M(CpCo)_2(\mu_2\text{-}CO)_2(\mu_2\text{-}CH_2)$ only one of two positional isomers possible is formed upon reaction with diazomethane. The preferred isomer has the methylidene ligand bridging a Cp*M–CpCo edge. In the case M = Rh this effect is clearly not due to a thermodynamic preference of the Rh–Co over the Co–Co isomer since equilibration of the initial product produces roughly a 1:1 mixture at equilibrium [12]. A possible explanation for the initial kinetic preference for the Cp*M–Co edge is found when the mechanism of diazomethane addition is examined more closely. The first step in the reaction of a diazoalkane with a metal is generally believed to involve coordination of the diazoalkane via the terminal nitrogen atom. The most likely point of attack is the Cp*M fragment despite the sterically demanding Cp* ligand because in the original $46e^-$ cluster complexes the two CO ligands are bound in a semitriply-bridging fashion over the CpCo–CpCo edge [15,30]. From this intermediate, the two products result from either moving the nitrogen to a triply bridging position with loss of one CO ligand or having the methylene group of diazomethane coordinate to one of the adjacent metal atoms forming a N–N–C bridge across the M–Co bond. Loss of dinitrogen from this species would then give the final methylidene product where the methylidene ligand bridges the M–Co bond. Such an intermediate involving a terminal diazomethane ligand has yet to be observed, but in the case of addition of carbon monoxide to the Ir containing $46e^-$ complex, the tricarbonyl complex $Cp^{*}Ir(CO)(CpCo)_2(\mu_2\text{-}CO)_2$ is isolated containing one terminally coordinated carbonyl ligand on iridium and two CO ligands bridging the Co–Co bond [15].

In both the Rh and Ir containing complexes **4** and **6**, the methylidene ligand migrates between the two Cp*M–CpCo edges interconverting the two the enantiomers of this positional isomer. Above 350 K this migration is fast enough to be monitored by magnetization transfer techniques such as NOESY spectroscopy. A similar process is observed in the all CpCo containing complex **1** where the methylidene ligand moves about the different Co–Co edges.

4. Summary

In rounding out our study of the reactions of diazoalkanes with Cp-based trinuclear clusters containing cobalt, rhodium and iridium we have found that in a limited number of cases alkylidene complexes result but that hydrazone containing products predominate, especially when only cobalt is involved. Alkylidene complexes are observed when iridium or rhodium is present, when only Cp ligands are involved in the case of tricobalt clusters and when the diazoalkane does not bear any substituents larger than hydrogen. In all cases studied, the initial alkylidene cluster product has this ligand bridging the Cp*M–CoCp edge. NMR evidence for migration of a methylidene ligand between Cp*M–CoCp edges has been observed in several complexes. In the cases of the cobalt (**1**) and iridium (**6**) analogues, activation parameters have been recorded which are similar to those observed for the rhodium complex [12], but no intermediates have been observed.

5. Experimental

All solvents were reagent grade and distilled from Na/K or CaH_2 under nitrogen to ensure oxygen free and dry conditions for all syntheses and chromatography. Air sensitive compounds were handled under nitrogen using Schlenk techniques or in a helium glove box. Column chromatography using degassed silica and solvents under nitrogen was used to purify the reaction products. The unsaturated dicarbonyl complexes of the form $(Cp^{*}M)(CpCo)_2(CO)_2$ (M = Co, Rh, Ir) were prepared as described by Barnes et al. [15]. $(CpCo)_3(CO)_2$ was prepared according to Barnes et al. [33]. Tetramethyl-trifluoromethylcyclopentadiene cobalt dicarbonyl $Cp^{\ddagger}Co(CO)_2$ was prepared as described by Gassman et al. and Vierkötter [28,34]. NMR spectra were recorded on a Bruker AMX-400 instrument. Reference signals used: C_6D_6: 7.15 ppm (^1H); 128 ppm (^{13}C); CD_2Cl_2: 5.32 ppm (^1H); 53.8 ppm (^{13}C). Diazomethane was prepared from Diazald® (Aldrich) was prepared as described in the Aldrich technical bulletin [35]. Diazoethane was prepared from 1-ethyl-1-nitroso-3-nitroguanadine and KOH in a water–ether mixed solvent system at 0°C. The yellow ether solution of diazoethane was stored overnight over KOH at −78°C and used without further purification.

Caution: *Low molecular weight diazoalkane compounds are extremely toxic, volatile and prone to explosive detonation when concentrated from solution. All manipulations of diazoalkanes must be performed in a well-ventilated hood. Furthermore, care should be taken to avoid concentrating diazoalkane solutions. All reactions described here involved dilute (> 0.1 M) ether solutions of the diazoalkane. Any excess diazoalkane from these reactions was decomposed by mixing with 0.1 M aqueous HCl solutions.*

5.1. General procedure for the reaction of diazoalkanes with unsaturated trinuclear clusters, $(Cp'M)(CpCo)_2(CO)_2$

In a glove box, between 200 and 500 mg of the dicarbonyl cluster complex was dissolved in ether in a Schlenk flask. Outside the glove box, the container were attached to a vacuum/nitrogen line and the solution frozen in liquid nitrogen. While purging with nitrogen, an ether solution of the diazoalkane (two- to threefold excess) was added. The solution was allowed to melt and warm to room temperature under a slow nitrogen purge. All volatile components of the reactions were then removed under vacuum and the residue transferred to top of a silica gel column under nitrogen for separation of the products.

All methylidene cluster complexes were eluted with ~1:1 mixtures of hexane–methylene chloride while hydrazone products were obtained with 10:1 mixtures of hexane–ether. Final recrystallizations were performed in mixtures of hexane–methylene chloride at low temperature. Combined yields of the purified products were between 30 and 50% based on the starting trinuclear complex. Spectroscopic and analysis data are summarized in Tables 2, 4–6.

*5.2. Crystal structures of **1** and **2***

Crystals for the structure determinations of complexes **1** and **2** were obtained at low temperature (-20°C) from hexane–methylene chloride. Data collection was performed on a R3m/V diffractometer at r.t. using Mo–K_α radiation (0.71073 Å). The SHELXTL suite of programs was used develop initial solutions and refine final structural models for **1** and **2**. In the case of the methylidene complex **1**, the carbonyl and methylidene ligands were found to be disordered. Although the hydrogen atom positions for the methylidene ligand were clearly seen in difference Fourier maps, a separate point of electron density was also observed ~1.18 Å from the carbon on the mirror plane for the complex, midway between the hydrogens. This was modeled as the oxygen atom of a disordered carbonyl ligand superimposed on the methylidene ligand. The carbon atoms of both ligands could not be resolved. Refinement of the occupancy of a minor component CO ligand in this position versus the two other Co–Co edges gave rise to a value of 0.15. Evidence for the minor occupancy of the methylidene ligand on either of the Co–Co edges carrying carbonyl ligands was not observed. In the final refinement of the structure, the occupancies of the oxygen atoms in the three positions were fixed at 0.15, 0.925, 0.925. The Cp ring not bisected by the mirror plane through the complex was constrained to be planar with the lengths of all C–C bonds restrained to be within 0.02 Å of each other in the model.

6. Supplementary material

Summaries of data collection parameters and final bond lengths, angles and thermal parameters are found in Tables 1–12 of the supplementary material to this manuscript.

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