ORGANOMETALLICS

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Organometallics, **1983**, 2 (6), 705-709• DOI: 10.1021/om00078a002 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street
N.W., Washington, DC 20036

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Reactions of (η^5-Cyclopentadienyl)ruthenium Isocyanide Complexes with Primary and Secondary Amines

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Received September 9, 1982

Methylamine and dimethylamine react with cyclopentadienylruthenium isocyanides to yield disubstituted and trisubstituted diaminocarbene complexes, respectively. Products included mono- and bis(carbene) complexes as well as chelated species of the form $\mathrm{Cp}\overline{\mathrm{Ru}[\mathrm{C(NHMe)(NMe)C}}\mathrm{(NMeR)](CO)(CNMe)^+}$ where R = H and Me. Significant differences in the identity and stability of the ruthenium products relative to analogous iron reactions have been observed. Rotational free energy barriers and isomeric preferences are also discussed.

Introduction

The formation of diaminocarbene ligands by the nucleophilic attack of primary and secondary amines on metal-coordinated isocyanides is a well-known process. We have recently reported an analysis of structural and rotational isomeric preferences that accompany such reactions in the iron isocyanide system $\mathrm{CpFe(CO)L)(CNR)^+}$ where L = $\mathrm{CN^-}$, CNR′, or $\mathrm{PR''_3}$.[2,3] The identities of metal and carbene substituents were found to have a significant effect on the relative populations of both types of isomers. Thermodynamic stabilities of the diaminocarbenes also varied, with the trisubstituted species in particular showing only marginal stability. A chelated intermediate was proposed to account for structural isomerization but was not observed under the reported reaction conditions. The effect of the metal itself on the kinetic and thermodynamic aspects of diaminocarbene formation was not identified. However, recent isolation of $\mathrm{K[CpRu(CO)(CN)_2]}$ and its alkylated products[4] has now permitted us to examine selected analogous ruthenium reactions. Significant differences in the structural compositions and stabilities of products in the ruthenium system have been determined and provide the basis for this paper.

Results and Discussion

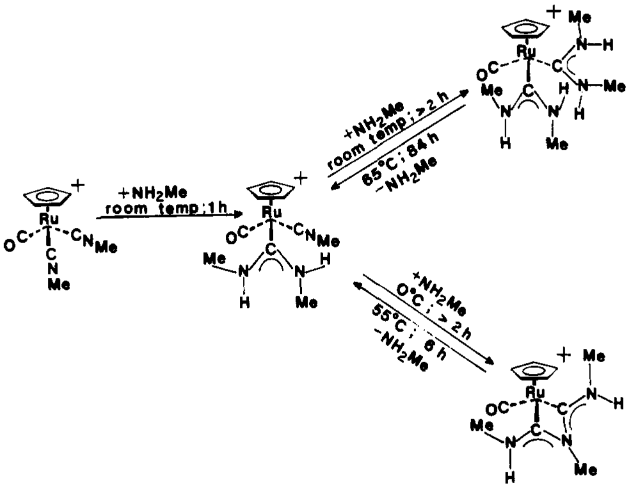
Reactions of $\mathrm{MeNH_2}$ and $\mathrm{Me_2NH}$ with CpRu(CO)(CN)(CNMe). Both primary and secondary methylamines reacted with the neutral monoisocyanide complex to produce disubstituted and trisubstituted carbenes:

$$\mathrm{CpRu(CO)(CN)(CNMe)} \xrightarrow{\mathrm{MeNH_2}} \mathrm{CpRu(CO)(CN)[C(NHMe)_2]} \tag{1}$$

$$\mathrm{CpRu(CO)(CN)(CNMe)} \xrightleftharpoons{\mathrm{Me_2NH}} \mathrm{CpRu(CO)(CN)[C(NHMe)(NMe_2)]} \tag{2}$$

The products were identified from their infrared and ^{1}H NMR spectra (summarized in Tables I and II) which were virtually identical with those of their iron analogues. The disubstituted ruthenium carbene complex was a stable white crystalline solid whose composition was also verified by elemental analysis (see Experimental Section). The trisubstituted carbene complex was too unstable to be isolated pure; however, NMR spectra indicated that in a 50/50 solution of methanol and the amine at 0 °C reaction 2 reached equilibrium with approximately 80% conversion to the carbene, compared to a maximum of 50% conversion in the iron system. When excess amine was removed dimethylamine was released, regenerating the initial isocyanide complex. At 27 °C the carbene complex displayed a half-life in solution of 2.64×10^3 s—almost 3 times that of $\mathrm{CpFe(CO)(CN)[C(NHMe)(NMe_2)]}$ (see Table III and ref 3).

Scheme I. Effect of Reaction Conditions on Predominant Product of Methylamine Reaction with $\mathrm{[CpRu(CO)(CNMe)_2]PF_6}$



Reactions of $\mathrm{MeNH_2}$ and $\mathrm{Me_2NH}$ with $\mathrm{CpRu(CO)(CNMe)_2{}^+}$. The reaction of the ruthenium bis(isocyanide) complex with excess methylamine was surprising in that three products were detected. Further, it was discovered that the proportion of the products could be largely controlled by adjusting the reaction conditions, facilitating the isolation of individual compounds. Conditions under which each of the three products predominated are shown in Scheme I.

The first of the three complexes to be isolated was $\mathrm{CpRu(CO)(CNMe)[C(NHMe)_2]^+}$, easily identified by its IR and ^{1}H NMR spectra (Tables I and II) which compare favorably with those of $\mathrm{CpFe(CO)(CNMe)[C(NHMe)_2]^+}$. When the reaction with methylamine was conducted at

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[1] Amoco Chemicals Corp., Naperville, IL 60566.

[2] B. V. Johnson, D. P. Sturtzel, and J. E. Shade, *J. Organomet. Chem.*, 154, 89 (1978).

[3] B. V. Johnson and J. E. Shade, *J. Organomet. Chem.*, 79, 357 (1979).

[4] Details of these preparations are described in a manuscript accepted for publication in *Synth. React. Inorg. Met.-Org. Chem.*

[5] Reaction conditions used to isolate the three components as reported in the Experimental Section were designed to minimize separation difficulties and differ somewhat from those in Scheme I.

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Table I. Infrared Spectra in C≡O and C≡N Stretching Regions[a]

compd	ν(C≡O), cm^{-1}	ν(C≡N), cm^{-1}	ν(C≡NMe), cm^{-1}
CpRu(CO)(CN)[C(NHMe)$_2$]	1961	2089	
CpRu(CO)(CN)[C(NHMe)(NMe$_2$)]	1955	2091	
CpRu(CO)(CNMe)[C(NHMe)$_2$]$^+$	1986		2206
CpRu(CO)[C(NHMe)$_2$]$_2$$^+$	1943		
CpRu(CO)[C(NHMe)(NMe)C(NHMe)]$^+$	1971		
CpRu(CO)(CNMe)[C(NHMe)(NMe$_2$)]$^+$	1988		2198
CpRu(CO)[C(NHMe)(NMe)C(NMe$_2$)]$^+$	1969		
CpRu(CO)[C(NMe)(NMe)C(NMe$_2$)]	1918		
CpRu(CNMe)$_2$[C(NHMe)$_2$]$^+$			2181, 2142
CpRu(CNMe)[C(NHMe)$_2$]$_2$$^+$			2120
CpFe(CO)[C(NHMe)(NMe)C(NHMe)]$^+$	1962		

[a] Spectra recorded in CH$_2$Cl$_2$.

Table II. Proton Nuclear Magnetic Resonance Data[a]

compd	diaminocarbene[b]	other ligands
CpRu(CO)(CN)[C(NHMe)$_2$]	3.10 d (4.5) NH*CH*$_3$ 2.91 d (4.8) NH*CH*$_3$	5.09 s Cp
CpRu(CO)(CN)[C(NHMe)NMe$_2$)]	3.32 s N(CH$_3$)$_2$ 3.23 d (4.5) NH*CH*$_3$	5.11 s Cp
CpRu(CO)(CNMe)[C(NHMe)$_2$]$^+$	3.15 d (4.6) NH*CH*$_3$ 2.92 d (5.1) NH*CH*$_3$	5.31 s Cp 3.65 s NCH$_3$
CpRu(CO)[C(NHMe)$_2$]$_2$$^+$	3.02 d (4.5) NH*CH*$_3$ 2.92 d (5.0) NH*CH*$_3$	5.31 s Cp
CpRu(CO)[C(NHMe)(NMe)C(NHMe)]$^+$	3.32 s NH*CH*$_3$ 3.17 s NCH$_3$	5.30 s Cp
CpRu(CO)(CNMe)[C(NHMe)(NMe$_2$)]$^+$	3.36 s N(CH$_3$)$_2$ 3.20 d (4.8) NH*CH*$_3$	5.50 s Cp 3.65 s NCH$_3$
CpRu(CO)[C(NHMe)(NMe)C(NMe$_2$)]$^{+c}$	3.27 s NH*CH*$_3$ 3.23 s NCH$_3$ $\left.\begin{array}{l}3.47\text{ s}\\3.42\text{ s}\end{array}\right\}\mathrm{N(CH_3)_2}$	5.11 s Cp
CpRu(CO)[(C(NMe)(NMe)C(NMe$_2$)]	3.33 s NCH$_3$ 3.19 s NCH$_3$ 3.54 s N(CH$_3$)$_2$	5.19 s Cp
CpRu(CNMe)$_2$[C(NHMe)$_2$]$^+$	3.13 d (4.5) NH*CH*$_3$ 2.87 d (4.9) NH*CH*$_3$	5.03 s Cp 3.52 s NCH$_3$
CpRu(CNMe)[C(NHMe)$_2$]$_2$$^+$	2.98 d (3.2) NH*CH*$_3$ 2.86 d (2.5) NH*CH*$_3$	4.93 s Cp 3.47 NCH$_3$
CpFe(CO)[C(NHMe)(NMe)C(NHMe)]$^+$	3.30 s NH*CH*$_3$ 3.06 s NCH$_3$	4.88 Cp

[a] Chemical shifts (δ) relative to Me$_4$Si in acetone-d_6 unless otherwise noted. [b] Splittings are given in hertz as follows: s, singlet; d, doublet; t, triplet; m, multiplet. NH protons are not included in the table but were generally observed as broad signals in the region 8.5–7.0 ppm. [c] Recorded in CD$_2$Cl$_2$.

Table III. Relative Stabilities of Iron and Ruthenium Diaminocarbenes[a]

		$T_{1/2}$, s		
compd	T, K	Ru	Fe	decomp product
CpM(CO)(CN)[C(NHMe)(CNMe$_2$)]	300	2.64 × 10^3	900	CpM(CO)(CN)(CNMe)
CpM(CO)(CN)[C(NHMe)(CNMe$_2$)]	330	78	30	CpM(CO)(CN)(CNMe)
CpM(CO)(CNMe)[C(NHMe)(NMe$_2$)]$^+$	330	720	240	CpM(CO)(CNMe)$_2$$^+$
CpM(CO)[C(NHMe)(NMe)C(NHMe)]$^+$	330	1.71 × 10^4	144	CpM(CO)(CNMe)[C(NHMe)$_2$]$^+$

[a] Decomposition half-life values were obtained by integration of cyclopentadienyl ^{1}H NMR resonances using CH$_2$Cl$_2$ as an internal concentration reference and assumed first-order rate behavior.

room temperature with reaction times of 1–2 h, this complex was the major component of the product mixture.

When the same reaction was allowed to proceed for longer periods, the predominant species was CpRu(CO)[C(NHMe)$_2$]$_2$$^+$, the first example of a bis(carbene) complex that we have observed in this type of cyclopentadienylmetal system. The infrared spectrum of the complex contained a single CO stretching band at 1943 cm^{-1}—a low frequency for a cationic complex environment, but consistent with the strong σ-donor capacity of the diaminocarbene ligand observed in our previous studies.[6] The ^{1}H NMR spectrum of the bis(carbene) complex exhibited the typical pattern of doublets observed for the nitrogen-bonded methyl protons in the monocarbenes (Table II), but the integrated area of these protons was 2.4 times that of the five cyclopentadienyl protons. This complex was both air stable and thermally robust, requiring several days reflux in methanol to revert to the monocarbene.

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When the reaction with methylamine was maintained at 0 °C, the chelated species $\mathrm{CpRu(CO)[C(NHMe)(NMe)C(NHMe)]^+}$ was obtained as the major product. In addition to the disappearance of the CNMe stretching band, the infrared spectrum of this complex displayed a single carbonyl frequency at 1971 $\mathrm{cm^{-1}}$, midway between those of the mono- and bis(carbene) compounds. The ^{1}H NMR of the compound in the carbene region produced two singlets in a ratio 2:1, representing the terminal and central carbons of the metallocycle. Integration was consistent relative to the five-proton cyclopentadienyl signal, and the equivalence of the two terminal methyl groups, as well as the lack of coupling to the nitrogen-bonded protons, parallels a description of the spectrum of the same bidentate group in $\mathrm{(OC)_4Mn[C(NHMe)(NMe)C(NHMe)]^+}$.[7] When excess amine was removed and the temperature of the solution increased to 55 °C, the chelate was observed to undergo ring opening, producing the mono(carbene) complex described above. The process could be reversed by the addition of excess dimethylamine. Identical interconversions have been noted in an octahedral iron isocyanide system, where $\mathrm{(CNMe)_4Fe[C(NHMe)(NMe)C(NHMe)]^{+2}}$ and $\mathrm{(CNMe)_5Fe[C(NHMe)_2]^{+2}}$ exist in equilibrium in excess amine.[8] Under room-temperature conditions and excess amine the ruthenium bis(carbene) could be obtained from solutions of either the mono(carbene) or the chelate, but in both cases the reaction probably occurs by attack of the amine on the free isocyanide of the mono(carbene). Recent findings indicate that attack at a carbene carbon of an aminocarbene is unlikely.[9] Satisfactory elemental analyses of all three products of $\mathrm{CpRu(CO)(CNMe)_2^+}$ and methylamine were obtained.

Formation of the chelated complex by base-catalyzed ring closure and isolation of the pure substance were of particular interest because $\mathrm{CpFe(CO)[C(NHMe)(NMe)C(NHR)]^+}$ (R = Et, *i*-Pr, *t*-Bu) had been proposed (but not observed) as an intermediate in the structural isomerization of $\mathrm{CpFe(CO)(CNMe)[C(NHMe)(NHR)]^+}$ to $\mathrm{CpFe(CO)(CNR)[C(NHMe)_2]^+}$.[2] The reaction of $\mathrm{CpFe(CO)(CNMe)_2^+}$ with methylamine also failed to give evidence of any products other than the mono(carbene) complex, though the ambient-temperature reaction conditions were probably too severe. Careful reexamination of this reaction at 0 °C produced spectroscopic evidence for the formation of $\mathrm{CpFe(CO)[C(NHMe)(NMe)C(NHMe)]^+}$ as reported in Table I and II. However, the decomposition half-life of the iron-chelated carbene was over 100 times shorter than that of the ruthenium complex (Table III), and consequently it could not be isolated.

The reaction of $\mathrm{CpRu(CO)(CNMe)_2^+}$ with dimethylamine produced the cationic trisubstituted diaminocarbene complex $\mathrm{CpRu(CO)(CNMe)[C(NHMe)(NMe_2)]^+}$. As expected, the product tended to revert to the starting isocyanide but at a much slower rate than did the iron complex (Table III). Under low-temperature conditions an analytically pure sample was obtained. In contrast to the iron system, extension of this reaction (at 0 °C) led to the isolation of a second product that had no CNR bands and one CO stretching band at 1969 $\mathrm{cm^{-1}}$. The ^{1}H NMR spectrum of this compound contained five singlets at 5.11 (Cp), 3.47, 3.42, 3.27, and 3.23 ppm in a ration of 5:3:3:3:3, compatible with the chelate structure $\mathrm{CpRu(CO)[C(NHMe)(NMe)C(NMe_2)]^3}$. Elemental analysis of the isolated substance was also consistent with this structure. Surprisingly, the trisubstituted chelate complex was considerably more stable than the disubstituted chelate described above. Further, a third product believed to be the deprotonated chelate $\mathrm{CpRu(CO)[C(NMe)(NMe)C(NMe_2)]}$ was also detected spectroscopically. The pattern of the ^{1}H NMR spectrum of this compound was nearly identical with the protonated chelate, but each of the resonances was shifted slightly upfield. There also was no evidence of an absorption attributable to NH protons that usually occurs as a broad signal in the region 8.5–7.0 ppm. Further, the infrared spectrum of this component exhibited a single carbonyl band at 1918 $\mathrm{cm^{-1}}$, a frequency more likely for an uncharged rather than a cationic complex. A similar deprotonated chelate $\mathrm{(CO)_4Mn[C(NHMe)(NMe)C(NMe)]}$ has been reported as a product of the reaction of $\mathrm{(CO)_4Mn[C(NHMe)(NMe)C(NHMe)]}$ and trimethylamine.[7]

Table IV. Estimated Rotational Free Energy Barriers[a]

compd	ΔG^* ($\pm$0.3 kcal/mol) M = Ru	M = Fe
$\mathrm{CpM(CO)(CN)[C(NHMe)_2]}$	16.8	17.3[b]
$\mathrm{CpM(CO)(CNMe)[NHMe)_2]^+}$	17.4	17.8[b]
$\mathrm{CpM(CO)[C(NHMe)_2]_2^+}$	17.1	
$\mathrm{CpM(CO)(CN)[C(NHMe)(NMe_2)]}$	13.4	
$\mathrm{CpM(CO)(CNMe)[C(NHMe)(NMe_2)]^+}$	14.3	14.1[c]
$\mathrm{CpM(CO)[C(NHMe)(NMe)C(NMe_2)]^+}$	18.5[d]	

[a] Calculated from 90-MHz ^{1}H spectra in acetone-d_6 unless otherwise noted. [b] See reference 1. [c] See reference 2. [d] Spectra recorded in $\mathrm{CD_2Cl_2}$.

Reaction of $\mathrm{MeNH_2}$ with $\mathrm{CpRu(CNMe)_3^+}$. The tris(isocyanide) reacted with methylamine to produce $\mathrm{CpRu(CNMe)_2[C(NHMe)_2]^+}$ as anticipated from reactions reported with iron tris(isocyanides).[6,10] However, unlike the iron systems, extended reaction of the ruthenium system in the presence of excess amine yielded a second product that eventually formed a 60:40 equilibrium mixture with the mono(carbene) complex. A single low-frequency CNR band was observed at 2120 $\mathrm{cm^{-1}}$ in the infrared spectrum. The second compound could not be separated from $\mathrm{CpRu(CNMe)_2[C(NHMe)_2]^+}$ but its ^{1}H NMR resonances could be identified at 4.93, 3.47, 2.98 and 2.86 ppm with the latter two occurring as doublets. This pattern, combined with integrated intensities of 5:3:6:6 strongly suggests the bicarbene $\mathrm{CpRu(CNMe)[C(NHMe)_2]_2^+}$. No evidence of chelate formation was detected.

Rotational Isomerism and Comparison of Fe and Ru Systems. The diaminocarbenes in this study were characterized by restricted rotation about the C–N bond. With the exception of the thermally unstable chelate $\mathrm{CpRu(CO)[C(NHMe)(NMe)C(NHMe)]^+}$, NMR spectra of each complex were found to be temperature dependent in that signals for methyl carbene substituents frozen in cis- or trans-to-metal positions broadened and coalesced

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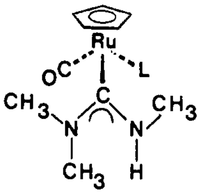

Figure 1. Preferred conformation of CpRu(CO)(L)[C(NHMe)(NMe$_2$)] complexes.

upon heating. As a result, rotational free energy barriers were measured by using methods that we have described previously.[2,3] Values obtained in this manner are listed in Table IV along with those of several analogous iron complexes. The metal identity apparently has a negligible effect on the rotational barrier with rotation most affected by introduction of a third carbene substituent, where diminished thermal stability is accompanied by a 3–4-kcal decrease in the free energy barrier. With regard to the trisubstituted chelate complex, only two of the methyl signals broadened upon heating, presumably those of the C–NMe$_2$ portion of the ligand. The barrier to rotation about this bond was calculated to be 18.5 kcal/mol–much larger than those found for the C–NMe$_2$ bond of trisubstituted mono(carbene) compounds. This effect is probably due to an increase in overlap between carbon and the exocyclic nitrogen that compensates for the decreased overlap resulting from the sharing by two carbons of the endocyclic nitrogen.

Two rotational isomers are possible in trisubsituted diaminocarbenes as the methyl group originating on the isocyanide can be cis or trans to the metal. Chemical shifts of this methyl occur in two narrow ranges that have been assigned to the cis and trans positions in the iron complexes.[3] The spectra in Table II show that the same ranges are observed in the disubstituted ruthenium carbenes. Therefore, the trisubstituted complexes CpRu(CO)(CN)[C(NHMe)(NMe$_2$)] and CpRu(CO)(CNMe)[C(NHMe)(NMe$_2$)]$^+$, on the basis of their ^{1}H NMR spectra, can be assigned the conformation seen in Figure 1. This conformation, which minimizes interior methyl carbene interactions, is also the only one observed in the iron carbene complexes.[3] The reduction in interior interactions is obtained at the expense of placing methyl groups in both cis-to-metal carbene positions, and the interaction of these groups with the cyclopentadienyl ring is believed to be the cause of the decreased stability of the trisubstituted complexes. Reports of gold and palladium systems having less crowded environments without cyclopentadienyl rings contain no mention of decreased stability for trisubstituted diaminocarbene ligands.[11,12] Longer metal–ring and metal–carbene distances in ruthenium complexes[13] most likely account for their increased stability vis-à-vis the iron derivatives.

Chelative addition, on the other hand, should favor the smaller metal ion,[14] but the opposite occurs in this system. It is noteworthy that both chelate and bis(carbene) formation are favored by ruthenium and both result in a considerable increase in electron density on the metal, as is evident by the decreases in carbonyl stretching frequencies. The greater capacity of ruthenium to accommodate strong σ-donating ligands appears to account for these differences. However, in CpRu(CNMe)$_3^+$, strong σ donation from three isocyanides instead of two apparently reduces the ability of the metal to stabilize a stronger σ-donating environment to the extent that the chelate structure is not observed at all and the bis(carbene) CpRu(CNMe)[C(NHMe)$_2$]$_2^+$ is significantly less stable than CpRu(CO)[C(NHMe)$_2$]$_2^+$.

Experimental Section

All reactions were conducted under an atmosphere of gaseous methylamine and dimethylamine. Low activity alumina (Fisher A-540) was employed for all chromatographic separations. THF was dried and deoxygenated by distillation from sodium benzophenone ketyl under nitrogen. All other chemicals and solvents were reagent grade and were used without further purification. All ^{1}H NMR spectra were recorded on a WH90-DS spectrometer equipped with a B-ST 100/700 variable-temperature accessory. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer calibrated with DCl. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN, and Guelph Laboratories, Ontario, Canada.

Preparation of Carbene Complexes. CpRu(CO)(CN)[C(NHMe)$_2$]. CpRu(CO)(CN)(CNMe)[4] (0.25 g, 1.0 mmol) was dissolved in 100 mL of methanol, and methylamine was bubbled through the solution at 0 °C for 3.5 h, during which time the solution volume doubled. After the solvents were removed, the residue was redissolved in acetone and filtered. Addition of ether caused the precipitation of the product as white crystals: yield 0.18 g (62%); mp 194–195 °C (Elemental Anal. Calcd for $C_{10}H_{13}N_3ORu$: C, 41.09; H, 4.48; N, 14.38. Found: C, 41.02; H, 4.22; N, 14.36).

CpRu(CO)(CN)[C(NHMe)(NMe$_2$)]. CpRu(CO)(CN)(CNMe)[4] (0.25 g, 1.0 mmol) was dissolved in 75 mL of methanol. This solution was treated for 3 h with dimethylamine at 0 °C (as above) until a 4/1 equilibrium with the starting isocyanide was reached. The solvents were removed in vacuo, maintaining the temperature below 0 °C at all times. The product was characterized by its infrared and ^{1}H NMR spectra (see Tables I and II) but was not separated from the isocyanide complex.

[CpRu(CO)(CNMe)[C(NHMe)$_2$]]PF$_6$. A suspension of (1.0 g, 2.4 mmol) [CpRu(CO)(CNMe)$_2$]PF$_6$[4] in 50 mL of methanol was treated with methylamine at 0 °C for 2 h. The solution was then placed in a pressure bottle and allowed to stir for an additional 2 h at room temperature. Methylamine and methanol were removed, and the residue was dissolved in acetone and refluxed for 6 h, converting any of the chelate complex present to the desired mono(carbene). After being heated, the solution contained only the mono- and bis(carbene) products. The mixture was chromatographed on alumina and the monocarbene eluted as a broad colorless band with 0.5% methanol in CH$_2$Cl$_2$. The solution was concentrated to 10 mL, ether was added to the point of precipitation, and large, white, rectangular crystals were allowed to form overnight: yield 0.47 g (44%); mp 120 °C (Elemental Anal. Calcd for $C_{11}H_{16}N_3ORuPF_6$: C, 29.21; H, 3.57; N, 9.29. Found: C, 29.20; H, 3.68; N, 9.14).

[CpRu(CO)[C(NHMe)$_2$]$_2$]PF$_6$. A solution of [CpRu(CO)(CNMe)$_2$]PF$_6$ (0.51 g, 1.2 mmol) in 80 mL of CH$_3$CN was treated with methylamine for 1 h without cooling. Removal of the solvents yielded a yellow oil that was chromatographed on alumina. The mono(carbene) present was eluted very slowly with CH$_2$Cl$_2$. The bis(carbene) was brought down as a colorless band with 3% methanol in CH$_2$Cl$_2$. The product was crystallized from CH$_2$Cl$_2$ by adding ether to the point of crystallization and then allowing the flask to stand at −15 °C overnight. The resulting white crystals were filtered and air dried; yield 0.11 g (22%); mp 140 °C (Elemental anal. Calcd for $C_{12}H_{21}N_4ORuPF_6$C, 29.82; H, 4.38; N, 11.59. Found: C, 29.97; H, 4.38; N, 11.56). (Higher yields could be obtained by extending the initial reaction time).

[Cp$\overline{\text{Ru(CO)[C(NHMe)(NMe)C}}$(NHMe)]]PF$_6$. [CpRu(CO)(CNMe)[C(NHMe)$_2$]PF$_6$ (0.12 g, 0.27 mmol) was dissolved in 10 mL of methanol. Dimethylamine was bubbled through for 1.5 h at 0 °C. The solvents were removed in vacuo, and the residue was dissolved in 5 mL of CH$_2$Cl$_2$. The addition of ether caused a pale oil to form which solidified on standing. It was collected

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and air-dried: yield 0.09 g (75%); mp 139 °C dec (Elemental Anal. Calcd for $C_{11}H_{16}N_3ORuPF_6$: C, 29.21; H, 3.57; N, 9.29. Found: C, 29.67; H, 3.73; N, 9.29).

[CpRu(CO)(CNMe)[C(NHMe)(NMe$_2$)]]PF$_6$. A solution of [CpRu(CO)(CNMe)$_2$]PF$_6$ (0.25 g, 0.63 mmol) in 100 mL of CH_3CN was treated for 45 min with dimethylamine at 0 °C. The solvents were removed, and the residue was crystallized from CH_2Cl_2 and diethyl ether at −15 °C. The white crystals were filtered and air-dried; yield 0.18 g (65%); mp 230 °C dec (Elemental Anal. Calcd for $C_{12}H_{18}N_3ORuPF_6$: C, 30.91, H, 3.89; N, 9.01. Found: C, 30.82; H, 3.89; N, 8.83).

[CpRu(CO)[C(NHMe)(NMe)C(NMe$_2$)]]PF$_6$. [CpRu(CO)(CNMe)$_2$]PF$_6$ (0.25 g, 0.63 mmol) was dissolved in 50 mL of CH_3CN. Dimethylamine was bubbled through this solution for 3 h at 0 °C. The reaction solution was transferred to a pressure bottle, and the reaction was continued at room temperature with stirring for 6 days. The solvents were then removed, and the residue was crystallized from CH_2Cl_2/diethyl ether. Off-white crystals formed and were collected on a filter and air-dried: yield 0.13 g (47%); mp 132 °C (melted with gas evolution, resolidified, and then melted again at 234 °C (melting point for [CpRu(CO)(CNMe)$_2$]PF$_3$)) (Elemental Anal. Calcd for $C_{12}H_{18}N_3ORuPF_6$: C, 30.91; H, 3.89; N, 9.01. Found; C, 30.77; H, 3.93; N, 9.29).

CpRu(CO)[C(NMe)(NMe)C(NMe$_2$)]. This compound was detected in IR and ^1H NMR spectra of the above reaction mixture of CpRu(CO)(CNMe)$_2^+$ with $NHMe_2$. Attempts to isolate the compound led only to recovery of the protonated chelate and were not extensively pursued.

[CpRu(CNMe)$_2$[C(NHMe)$_2$]]PF$_6$. [CpRu(CNMe)$_3$]PF$_6$ (0.26 g, 0.60 mmol) was dissolved in 50 mL of CH_3CN, and the resulting solution was treated with methylamine at 0 °C for 4 h. Removal of the solvents yielded a gray residue that was chromatographed on alumina. The product was eluted with 2% methanol in CH_2Cl_2. It was obtained as white crystals from CH_2Cl_2 by the addition of diethyl ether: yield 0.21 g (75%); mp 174.5 °C (Elemental Anal. Calcd for $C_{12}H_{19}N_4RuPF_6$: C, 30.97; H, 4.12; N, 12.04. Found: C, 31.22; H, 4.16; N, 11.96).

[CpRu(CNMe)[C(NHMe)$_2$]$_2$]PF$_6$. [CpRu(CNMe)$_3$]PF$_6$ (0.25 g, 0.6 mmol) was dissolved in 50 mL of CH_3CN, and the resulting solution was treated with methylamine at 0 °C for 4 h. The solution was then placed in a pressure bottle and allowed to stir at room temperature for 3 days. The solution was then chilled to 0 °C, the solvents were evacuated, and the residue was washed with diethyl ether and stored at −20 °C. The product was detected and characterized by its infrared and ^1H NMR spectra. Attempts to separate this compound from the other reaction product CpRu(CNMe)$_2$[C(NHMe)$_2$]$^+$ were unsuccessful.

[CpFe(CO)[C(NHMe)(NMe)C(NMe)]]PF$_6$. [CpFe(CO)(CNMe)$_2$]PF$_6$[15] (0.25 g, 0.67 mmol) was dissolved in 25 mL of methanol, and methylamine was bubbled through the solution at 0 °C for 2.5 h. The reaction was stoppered and allowed to stir for two more hours at which point spectroscopic data indicated that the chelate product had formed (Tables I and II). Attempts to crystallize the product, even at low temperatures, resulted in the conversion of the product to CpFe(CO)(CNMe)[C(NHMe)$_2$]$^+$.

Registry No. CpRu(CO)(CN)[C(NHMe)$_2$], 84987-34-8; CpRu(CO)(CN)[C(NHMe)(NMe$_2$)], 84987-35-9; [CpRu(CO)(CNMe)[C(NHMe)$_2$]]PF$_6$, 84987-37-1; [CpRu(CO)[C(NHMe)$_2$]$_2$]PF$_6$, 84987-39-3; [CpRu(CO)[C(NHMe)(NMe)C(NHMe)]]PF$_6$, 84987-41-7; [CpRu(CO)(CNMe)[C(NHMe)(NMe$_2$)]]PF$_6$, 84987-43-9; [CpRu(CO)[C(NHMe)(NMe)C(NMe$_2$)]]PF$_6$, 84987-45-1; CpRu(CO)[C(NMe)C(NMe$_2$)], 84987-46-2; [CpRu(CNMe)$_2$[C(NHMe)$_2$]]PF$_6$, 84987-48-4; [CpRu(CNMe)[C(NHMe)$_2$]$_2$]PF$_6$, 84987-50-8; [CpFe(CO)[C(NHMe)(NMe)C(NHMe)]]PF$_6$, 84987-52-0; CpRu(CO)(CN)(CNMe), 84987-53-1; [CpRu(CO)(CNMe)$_2$]PF$_6$, 84987-55-3; [CpRu(CNMe)$_3$]PF$_6$, 84987-57-5; [CpFe(CO)(CNMe)$_2$]PF$_6$, 70130-45-9; CpFe(CO)(CNMe)[C(NHMe)$_2$]$^+$, 52409-95-7; $MeNH_2$, 74-89-5; Me_2NH, 124-40-3.

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Synthesis of Organosamarium Complexes Containing Sm–C and Sm–P Bonds. Crystallographic Characterization of $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$[1]

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Received September 9, 1982

$[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$, I, has been synthesized from $(CH_3C_5H_4)_2SmCl(THF)$ and $LiC{\equiv}CC(CH_3)_3$ in THF and characterized by spectroscopic, analytical, and crystallographic methods. I crystallizes from toluene at 0 °C in the monoclinic space group $P2_1/c$ with unit-cell dimensions a = 9.418 (3) Å, b = 17.830 (6) Å, c = 11.134 (5) Å, β = 113.10 (3)°, and Z = 2 (dimers) for D_{calcd} = 1.51 g cm^{-3}. Full-matrix least-squares refinement led to a final R value of 0.048 on the basis of 1659 observed reflections. The two $(CH_3C_5H_4)_2Sm$ units in the dimer are connected by electron-deficient alkynyl bridges that have Sm–C distances of 2.55 (1) Å and asymmetric Sm—C≡C angles of 151 (1) and 122 (1)°. The reaction of I with $HP(C_6H_5)_2$ forms $HC{\equiv}CC(CH_3)_3$ and $(CH_3C_5H_4)_2SmP(C_6H_5)_2$, II, which has been characterized by spectroscopic and analytical methods.

Introduction

Traditionally, the two most important factors affecting the stability of organometallic complexes of the lanthanides are optimization of electrostatic interactions and saturation of the coordination sphere of the metal with bulky ligands in order to sterically block decomposition pathways.[3] A consequence of the latter feature is that the elements occurring later in the series, particularly Er, Yb, and Lu, are used more frequently in synthesis, since it is less difficult

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(1) Presented in part at the: "1982 American Chemical Society Division of Inorganic Chemistry Biennial Symposium", Bloomington, IN, May 1982; American Chemical Society: Washington, DC, 1982; C15.

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0276-7333/83/2302-0709$01.50/0