pathways in the reactions of concern are noteworthy. The Beckmann fragmentations, in particular, occur rapidly under mild conditions and proceed in high yields; these factors attest to the utility of the process in synthetic chemistry.

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Carbene Ligand Insertion into a Metallacycle Ring: A Metallacyclopentadiene to Metallacyclobutene Conversion

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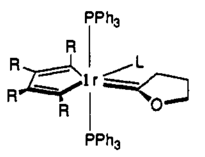
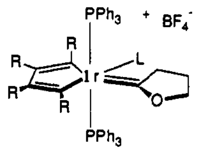
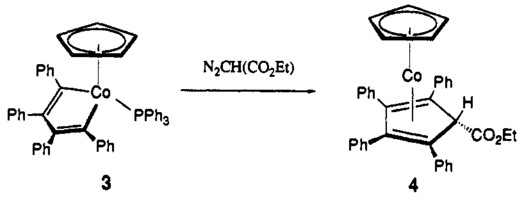


1, L = Cl, F

R = CO_2CH_3



2, L = CO, OH_2



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In an effort to couple the reactivity patterns of metal carbene and metallacycle complexes, we recently prepared the first examples of isolable, mononuclear metallacycle–carbene complexes, 1-L (L = Cl, F; R = CO_2CH_3) and 2-L (L = CO, H_2O; R = CO_2CH_3).[1] One specific goal in the synthesis of these complexes was to observe an unprecendented carbene ligand insertion into the metallacycle ring of a characterized metallacycle–carbene complex.[2] A reductive elimination from the resultant metallacyclohexadiene product would lead to a five-membered carbocycle. Indeed, we recently observed the reaction of cobalt metallacycles (e.g., 3) with ethyl diazoacetate to give cyclopentadiene products (e.g., 4).[3] This reaction may involve metallacycle–carbene intermediates. Intramolecular migratory coupling reactions of carbene and (sp^3) carbon ligands are precedented:[4] however, we are aware of only one mononuclear case that appears to involve a vinyl ligand–carbene ligand coupling.[5] In light of the ready accessibility of both carbene and metallacycle complexes, the development of metallacycle–carbene coupling reactions would represent significant new carbon–carbon bond formation methodology. Herein we report a novel metallacyclopentadiene to metallacyclobutene conversion,[6] which proceeds via carbene ligand insertion into the carbon–metal bond of a metallacycle.

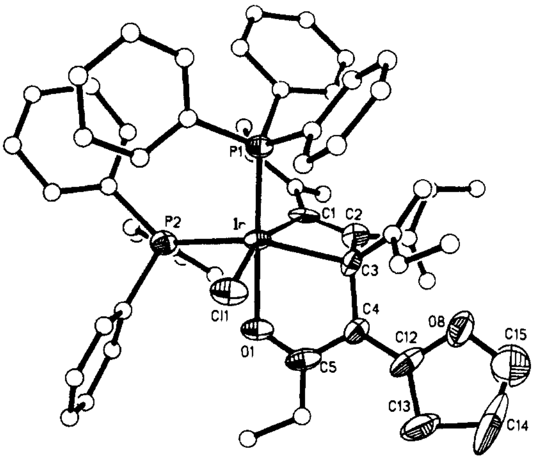
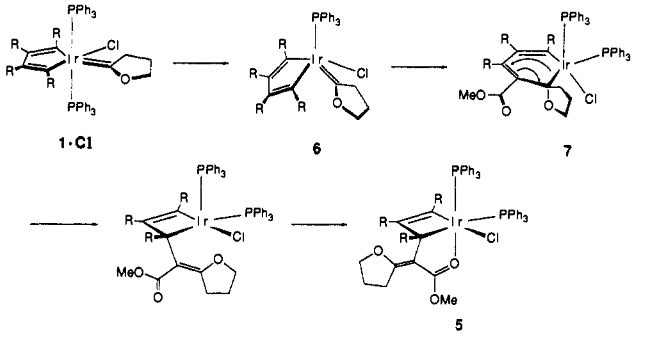


Figure 1.

Scheme I



When a chloroform-d_1 solution of the neutral metallacycle-carbene 1-Cl (0.13 M) is heated at 72 °C, the ^1H NMR resonances due to 1-Cl are gradually and quantitatively replaced by a new set of resonances, which arise from formation of iridiacyclobutene 5.[7] In the ^1H NMR spectrum of 5, four singlets (3 H each) are observed at δ 2.36, 2.55, 3.30, and 3.62, which are assigned to the hydrogens of four unique carboxymethyl groups. ^1H NMR resonances at δ 2.04 (m, 2 H), 3.10 (m, 2 H), and 4.24 (m, 2 H) are consistent with an intact oxacyclopentylidene ring; however, in the $^{13}C\{^1H\}$ NMR spectrum of 5, the farthest downfield resonance is at 187 ppm. Thus the carbene ligand in 1-Cl is no longer present in 5. A broad doublet at 18.22 (J = 67.6 Hz) ppm in the $^{13}C\{^1H\}$ NMR spectrum is consistent with an sp^3 carbon trans to a PPh_3 ligand. In the $^{31}P\{^1H\}$ NMR spectrum two doublets are observed at δ −10.9 (J = 10 Hz) and −23.9 (J = 10 Hz), indicative of nonequivalent cis PPh_3 ligands. The spectroscopic data are thus consistent with either an iridiacyclohexadiene structure or the actual iridiacyclobutene structure.

In order to unambiguously determine the structure of complex 5 a single-crystal X-ray diffraction study was performed (Figure 1).[8] The X-ray results indicate that a remarkable transformation

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(7) Complete spectroscopic and analytical data for 5, 2-H_2O, and 1-F are provided as supplementary material. Complex 2-H_2O was prepared by treatment of 1-Cl with $AgBF_4$ in wet CH_2Cl_2, and 1-F was prepared by treatment of 2-H_2O with KF in methylene chloride solution.

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has occurred. Most notably, the carbene carbon in **1**-Cl is now bonded directly to one of the α-carbons of the original metallacycle ring. In addition, the metallacyclopentadiene has undergone a novel ring contraction to a metallacyclobutene structure.[9] The largest deviation from the metallacycle mean plane is 0.0231 Å at C(2). The Ir-C(1) distance of 2.045 Å is similar to that observed for the related iridium-(sp^2)carbon distances in iridiacyclopentadiene complexes such as **2**-CO (2.101-2.161 Å).[1,10] The metallacycle bond distances also agree closely with those observed by Thorn for a related iridium(III) metallacyclobutene complex.[11]

The rate of reaction of **1**-Cl in $CDCl_3$ was monitored by ^1H NMR spectroscopy. In the presence of added PPh_3, the observed pseudo-first-order kinetics for conversion to **5** indicate an inverse dependence on the phosphine concentration.[12] The trans geometry of the carbene ligand and one of the α-metallacycle carbons in **1**-Cl prohibits a direct migration of the cis α-metallacycle carbon to the carbene ligand.[13] Phosphine dissociation, however, leads to an unsaturated intermediate, which may adopt a square-pyramidal geometry (**6**, Scheme I) from which a migration is feasible.[14] Migration and phosphine addition leads to a metallacyclohexadiene intermediate, **7**. A 1,3-shift of iridium and coordination of the methoxycarbonyl oxygen would then generate **5**.[15,16] Whether or not the reaction is chelate-assisted requires further investigation.

The thermal stability of the metallacycle-carbene complex depends greatly on the nature of the non-phosphine ligand. Thus, heating a chloroform solution of **2**-CO at 75 °C for 48 h results in only a trace of decomposition, with no evidence for metallacyclohexadiene or cyclopentadiene formation. The much more labile aquo complex **2**-H_2O decomposes in dry chloroform solution, even at 23 °C over the course of 3 days, to give a complex mixture of the products.[7,17] In wet chloroform **2**-H_2O is stable for more than 3 days under similar conditions. The neutral fluoro derivative **1**-F decomposes slowly at 75 °C and also gives a complex mixture of products.[7] Efforts are underway to prepare related metallacycle-carbene complexes that will lead to isolable metallacyclohexadiene products.

Acknowledgment. Support of the National Science Foundation (CHE-9005973) is gratefully acknowledged.

Supplementary Material Available: Full spectroscopic and analytical data for compounds **2**-H_2O, **1**-F, and **5**, listings of fractional coordinates, bond distances, bond angles, hydrogen atom coordinates, and thermal parameters (8 pages); table of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(8) Crystal data for **5** (296 K): $C_{52}H_{48}ClIrO_9P_2\cdot{}^1/_2CHCl_3$, triclinic $P\bar{1}$, $a = 10.209$ (3) Å, $b = 13.516$ (7) Å, $c = 19.888$ (7) Å, $\alpha = 83.57$ (4)°, $\beta = 84.85$ (3)°, $\gamma = 72.63$ (4)°, $V = 2598$ (2) Å^3, $Z = 2$, $D_{calc} = 1.491$ g cm^{-3}, $\mu = 28.0$ cm^{-1}. A platelike yellow specimen (0.06 × 0.23 × 0.31 mm) was used for data collection (Siemens R3m/V, 4.0° ≤ 2θ ≤ 45.0°, Mo Kα, 24-25 °C). Of 6784 reflections collected, 6478 were independent ($R_{int} = 0.00\%$) and 4926 with $F > 6.0\sigma(F)$ were considered observed and corrected for absorption by using face-indexed numerical method. ($T_{min}/T_{max} = 0.9475/0.9862$). The Ir atom was located by a heavy atom method. With all non-hydrogen atoms anisotropically refined and hydrogen atoms treated as riding model, fixed isotropic $U = 0.08$ Å^2: $R(F) = 5.88\%$, $R(wF) = 7.94\%$, all data $R(F) = 8.50\%$, GOF = 0.85, $\Delta/\sigma = 0.045$, $\Delta(\rho) = 2.62$ e A^{-3}. All computer programs and sources of scattering factors are contained in the SHELXTL program library (Siemens Corp., Madison, WI).

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(12) For [**1**-Cl] = 29.7 mM, [PPh_3] = 1.14 M, $k_{obs} = 1.15 \times 10^{-4}$ s^{-1}; [**1**-Cl] = 31.2 mM, [PPh_3] = 0.58 M, $k_{obs} = 2.67 \times 10^{-4}$ s^{-1}; [**1**-Cl] = 31.8 mM, [PPh_3] = 0.30 M, $k_{obs} = 4.13 \times 10^{-4}$ s^{-1}; [**1**-Cl] = 31.2 mM, [PPh_3] = 0.15 M, $k_{obs} = 7.73 \times 10^{-4}$ s^{-1}.

(13) By analogy to alkyl migration to a carbonyl ligand, carbene-alkyl coupling reactions presumably involve an alkyl migration to the carbene ligand rather than a carbene insertion into the metal-alkyl bond. Thorn has observed alkyl-carbene ligand couplings at iridium(III), which support an alkyl migration pathway: Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. Thorn, D. L. *Organometallics* **1985**, *4*, 192.

(14) Migration of the metallacycle carbon to the carbene ligand is geometrically feasible from either a square-pyramidal intermediate as shown for **6** or an octahedral bis(phosphine) complex with a facial arrangement of the three carbon-bound ligands. The required orthogonal carbene ligand orientation with respect to the metallacycle may be facilitated by loss of phosphine; however, a metallacycle migration to the carbene ligand will still require one of the above geometries.

(15) Metallacyclohexadiene complex **7** may exist as a 1,2,3,5-η-penta-2,4-dienediyl ligand in which one of the metallacycle double bonds is coordinated to the metal. The 1,3 iridium shift would then be described as an η^3 to η^1 rearrangement of a π-allyl intermediate: Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1578. Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.: Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1694. Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576.

(16) We cannot completely exclude a mechanism involving metallacycle reversion to two alkynes, with subsequent alkyne-carbene coupling. Thermolysis of **1** at 75 °C in the presence of excess dimethyl acetylenedicarboxylate-d_6 leads to catalytic formation of hexa(carboxymethyl)benzene, **8**-d_n. Compound **1** decomposes under these conditions and no identifiable iridium-containing products are observed (by ^1H NMR spectroscopy). The partially labeled **8**-d_n is 10% d_{12} and 90% d_6. This *may* be indicative of a minor amount of metallacycle reversion under these conditions.

(17) **2**-H_2O decomposes in dry chloroform-d_1 at 23 °C over the course of 3 days to give a number of decomposition products in addition to one major prouct in 39% yield (by ^1H NMR spectroscopy). This product was not isolated, but spectroscopy on the crude reaction mixture indicated nonequivalent cis PPh_3 ligands [^{31}P NMR: δ -25.38 (d, $J = 11$ Hz) and -2.2 (br d, $J = 11$ Hz)] as was observed for **5**.

Incremental Preorganization of a Chelating Macrocycle

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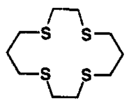
Complexation of the environmentally and economically important late-transition-metal ions by polythioethers has been studied in many laboratories.[1] Surprisingly, however, relatively little effort has been devoted to exploring how changes in polythioether structure affect the strength and specificity with which thiophilic metal ions are bound, particularly in comparison with the large body of work on optimization of poly*oxo*ether complexing agents for oxophilic cations.[2] We now report that simple peripheral modifications of a macrocyclic tetrathioether can have a substantial impact on chelation efficacy. A comparison of structural and solution data on Ni(II) binding by tetrathiothers **1**-**3**[3] reveals that successive additions of appropriately placed *gem*-dimethyl groups induce macrocycle conformations that are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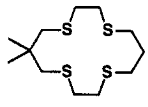
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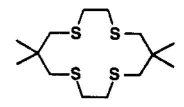
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