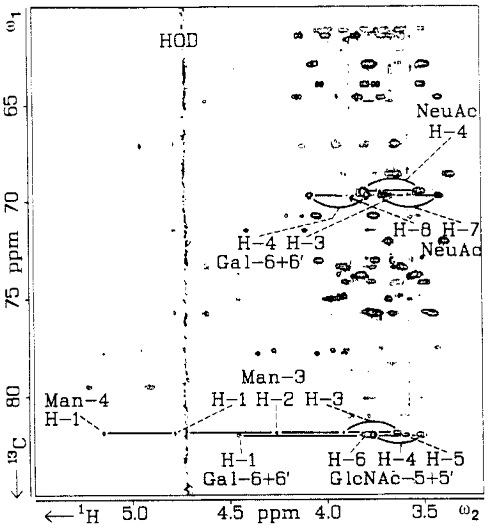

Figure 3. The bulk region of a 2D HMQC-NOE $^1H/^{13}C$ spectrum of a 20 mM solution of **1** in D_2O at 304 K and pH 7. The phase-sensitive spectrum was recorded at 500 MHz on a Bruker AM500 spectrometer. Acquisition was preceded by four dummy scans; 2048 t_1 increments of 48 scans each were recorded at a size of 2 K, resulting in a total measuring time of approximately 60 h. The relaxation delay was 1.0 s; Δ was 1.78 ms. Spectral width in the ^1H time domains was 2272.7 Hz and, in the ^{13}C time domain, 11 364 Hz. The NOE mixing time was 0.35 s. Cosine multiplications were used in the t_2 and t_1 domains. The resulting data set after Fourier transformation of 1024 × 1024 points was baseline-corrected in both frequency domains by a fourth-order polynomial fit.

between NeuAc H-6 and H-7 prevents magnetization transfer by the isotropic mixing to the well-resolved NeuAc H-3 protons.

The extra ^1H dimension t_2 will separate protons attached to carbon atoms having the same ^{13}C chemical shift. If there is no overlap in the ^{13}C spectrum, this extra dimension is not necessary. The pulse sequence of 2D HMQC-NOE is identical with the 3D sequence except that the evolution period t_2 and the decoupling pulse have been left out. Most NOEs found in the 3D spectrum of **1** are also identified in the 2D spectrum of **1** (Figure 3). NOEs as discussed for the 3D spectrum in Figure 2, parts B and C, are indicated in Figure 3. For compounds with a well-resolved ^{13}C spectrum, the 2D HMQC-NOESY sequence is a good alternative for the 3D sequence. For the majority of NOEs in the 3D spectrum of **1**, the third dimension is only needed to compensate for the poor resolution in the ^{13}C direction as is shown for the GlcNAc-5/5′ H-4 and Man-3 H-3 in Figure 2B. With the higher resolution of the 2D HMQC-NOE (2048 t_1 increments) as compared to the 3D experiment (112 t_1 increments), the ^{13}C frequencies of GlcNAc-5/5′ C-4 and Man-3 C-3 are now resolved (Figure 3). The NOE between Gal-6 H-4 and Gal-6 H-5 as indicated in Figure 2C is an example of a cross peak, which cannot be identified in the 2D spectrum due to overlap of the ^{13}C frequencies of Gal-6 C-4, NeuAc C-4, and NeuAc C-7. Here the extra ^1H dimension is needed to resolve the overlap by using the difference in ^1H chemical shift of Gal-6 H-4, NeuAc H-4, and NeuAc H-7 (Figure 2C).

The present work illustrates the usefulness of heteronuclear 2D and 3D NMR techniques in structure elucidations of complex oligosaccharides. Although the spectra shown are recorded at natural abundance, the sensitivity is sufficient to identify most of the NOEs of **1**. Editing 2D NOE with respect to the carbon frequency gives a key to elucidating NOEs of any proton hidden in the bulk region.

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Mechanism of the C–C Cleavage of Acetone by the Ruthenium Benzyne Complex $(PMe_3)_4Ru(\eta^2\text{-}C_6H_4)$: Formation and Reactivity of an Oxametallacyclobutane Complex

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The reaction of acetone with the ruthenium benzyne complex $(PMe_3)_4Ru(\eta^2\text{-}C_6H_4)$ (**1**) results in cleavage of a C–C bond[1] in the ketone, leading to methane and **2**, an ortho-metalated enolate complex of acetophenone (Scheme I).[2] We now report the generation and spectroscopic characterization of a potential intermediate in this reaction: complex **3**, a rare example of an oxametallacyclobutane. This material is formed in an unusual transformation that involves overall β-migration of a phenyl group from ruthenium to carbon in a transition-metal enolate, followed by an apparent β-alkyl elimination reaction.[1f,g] Studies of the chemistry of complex **3** show that it undergoes a number of novel reactions, including several that involve fragmentation to α-methylstyrene.

The synthesis of oxametallacyclobutane complex **3** is shown in Scheme I. Solutions of enolate **5**, the expected product from the reaction of acetone with $(PMe_3)_4Ru(\eta^2\text{-}C_6H_4)$ (**1**), were prepared by treatment of benzyne complex **1** with Me_3NHCl (leading to *cis*- and trans-phenylchlororuthenium complexes **4**), followed by reaction with the potassium enolate of acetone.[3] Only the O-bound isomer was detected by ^1H and $^{31}P\{^1H\}$ NMR spectrometry at −20 °C, in contrast to most late-transition-metal enolates, which exist as the C-bound isomer.[4] At room temperature over the course of an hour, complex **5** rearranges by an intramolecular migration of the phenyl group to the unsaturated enolate substituent, to form oxametallacyclobutane complex **3**.[5,6]

Complex **3** exhibits a temperature-dependent ^1H NMR spectrum, presumably due to rapid, reversible dissociation of phosphine. Decomposition of **3**, due to irreversible dissociation of phosphine

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(1) For other examples of C–C activation reactions, see: (a) Suggs, J. W.; Cox, S. D. *J. Organomet. Chem.* **1981**, *221*, 199. (b) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, *106*, 3054. (c) Suggs J. W.; Wovkulich, M. J. *Organometallics* **1985**, *4*, 1101. (d) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1986**, *108*, 4679. (e) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (f) Crabtree, R. H.; Dion, R. P.; Gibbone, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222 and references therein. (g) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (h) Bunel, E.; Berger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976.

(2) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717.

(3) Room-temperature addition of acetone to a pentane/toluene solution of $KN(SiMe_3)_2$ precipitated $KOC(CH_2)Me$, which was collected by filtration and stored at −40 °C in the drybox for up to one week without noticeable decomposition.

(4) Only a few examples of late-transition-metal O-bound enolate complexes have been reported: (a) Ito, Y.; Nakatsuka, M.; Kise, N.; Saegusa, T. *Tetrahedron Lett.* **1980**, *21*, 2873. (b) Slough, G. A.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1989**, *111*, 938. An extensive list of late-transition-metal C-bound enolate complexes is included in this reference.

(5) Reversible insertion of a chelated olefin into a metal alkyl has been observed: Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076. Some intermolecular additions of nucleophiles to the center of π-allyl complexes have been observed: (a) Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; Mackenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131. (b) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7272.

(6) For previously reported oxametallacyclobutane complexes, see: (a) Scholdder, T.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Am. Chem. Soc.* **1974**, *96*, 6893. (b) Lenarda, M.; Ros, R.; Traverso, O.; Pitts, W. D.; Baddley, W. H.; Graziani, M. *Inorg. Chem.* **1977**, *16*, 3178. (c) Klein, D. P.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3704. (d) Ho, S. C.; Hentges, S.; Grubbs, R. H. *Organometallics* **1988**, *7*, 780. (e) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 6466. For oxametallacyclobutene complexes, see: (f) Vaughan, G. A.; Hillhouse, G. L.; Lum, R. T.; Buchwald, S. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 7215. (g) Vaughan, G. A.; Sofield, C. D.; Hillhoue, G. L. *J. Am. Chem. Soc.* **1989**, *111*, 5491.

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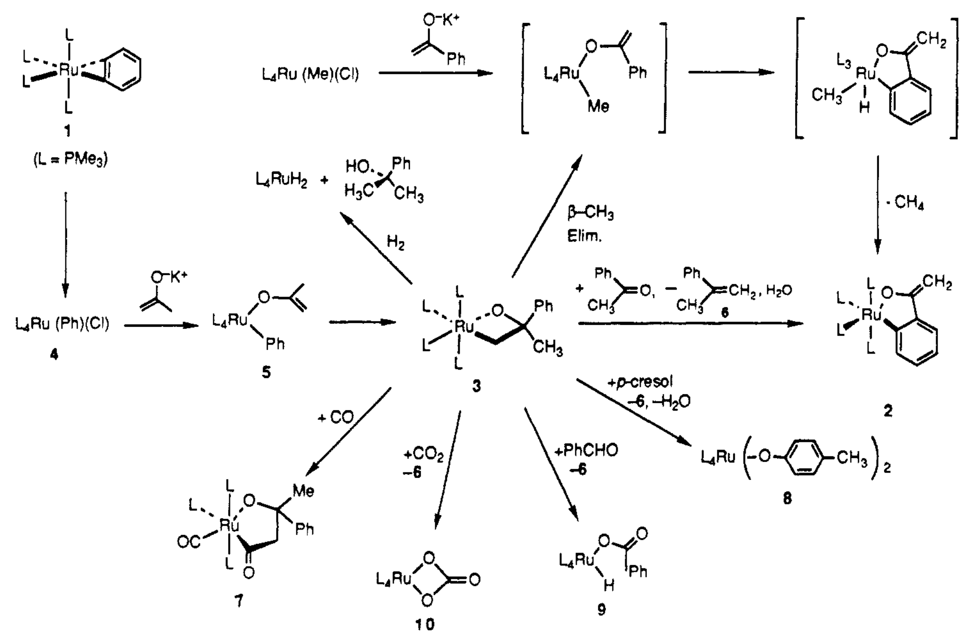
Scheme I



under vacuum and its very high solubility in aliphatic hydrocarbon solvents, has precluded isolation in crystalline form. However, its identity as an oxametallacyclobutane complex was established by the following spectral characteristics obtained at −40 °C:[7,8] (a) In contrast to **5**, the ^{1}H NMR spectrum of **3** displays an absence of olefinic resonances. (b) The ^{13}C{^{1}H} NMR spectrum of the material shows the ipso carbon of the aryl ring as a singlet, while the CH_2 group (assigned by 135° DEPT ^{13}C NMR spectroscopy) displays coupling to four phosphines, indicating that this carbon is now bound to the metal center. The ^{31}P{^{1}H} NMR spectrum of **3** exhibits an ABCD pattern, with one of the chemical shifts appearing in the region common for phosphines located trans to alkoxide linkages in other $(PMe_3)_4Ru$ compounds.[2] The connectivity of the metallacycle portion of **3** was confirmed by treatment of the complex with dihydrogen (2 atm), which gave $(PMe_3)_4Ru(H_2)$ in 88% yield and the tertiary alcohol $HOC(Me)_2(Ph)$ in 85% yield.[9]

Gentle heating of a benzene solution of **3** (8 h at 45 °C) led to formation of **2**[10] (51% yield by ^{1}H NMR spectroscopy) and methane, providing strong evidence that the reaction of the benzyne complex **1** with acetone proceeds through this intermediate. We believe that the C–C cleavage step in the conversion of **3** to **2** involves a β-methyl elimination reaction to form a methyl enolate complex, which undergoes ortho-metalation followed by reductive elimination to form **2** as shown in Scheme I. Addition of the potassium enolate of acetophenone to $(PMe_3)_4Ru(Me)(Cl)$ at room temperature provided **2** in 98% yield, confirming that such a methyl enolate intermediate would form **2** under the reaction conditions.

Oxametallacycle **3** exhibits other unusual reaction chemistry. For example, treatment of **3** with 2 atm of carbon monoxide led to immediate formation of the CO-inserted metallacycle **7** in 51% isolated yield. The greater propensity for insertion of CO into the metal–carbon rather than the metal–oxygen bond contrasts with the higher reactivity of the M–O bond in the similar iridium oxametallacycle $Cp^*Ir(PMe_3)(\eta^2\text{-}CH_2C(Me)_2O)$ reported earlier from this laboratory.[6c]

Metallacycle **3** displays clean reactivity with several protic acids and carbon electrophiles, and each reaction results in the extrusion of α-methylstyrene (**6**).[11] Thus, reaction of a benzene solution of **3** with acetophenone at 45 °C for 8 h led to α-methylstyrene and **2** in 61% yield (^{1}H NMR spectroscopy). Water was presumably a byproduct of this reaction although it could not be detected.[12] Reaction of a benzene solution of **3** with excess *p*-cresol at room temperature led to immediate formation of the bis(cresolate) complex **8** in 82% yield by ^{1}H NMR spectroscopy, α-methylstyrene in 86% yield, and again presumably water. The bis(cresolate) complex was prepared independently in 57% yield by the addition of 2 equiv of *p*-cresol to $(PMe_3)_4Ru(Me)_2$.

Treatment of **3** with benzaldehyde at room temperature immediately extruded the same alkene **6** in 73% yield along with the hydrido benzoate complex **9** in 53% yield by ^{1}H NMR spectroscopy. This complex was independently synthesized by the addition of benzoic acid to the ethylene complex $(PMe_3)_4Ru(\eta^2\text{-}C_2H_4)$[13] to give **9** (14% isolated yield) and ethylene. Reaction of **3** with carbon dioxide in benzene at room temperature rapidly precipitated the carbonate complex **10** in 83% yield. This material was independently synthesized in 85% isolated yield by the reaction of *trans*-$(PMe_3)_4Ru(Cl)_2$ with K_2CO_3 in methanol. The addition of styrene, 4′-methyl-α-methylstyrene, 2-butyne,

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(7) Solutions containing **3** in roughly 85% purity were generated, and **3** was used in situ. We were able to assign the resonances due to the metallacyclic portion of the molecule in the ^{1}H and ^{13}C{^{1}H} NMR spectra. Assignment of the PMe_3 resonances in the ^{1}H and ^{13}C{^{1}H} NMR spectra was ambiguous due to overlap with solvent and impurity resonances, but the four inequivalent phosphines were clearly observed in the ^{31}P{^{1}H} NMR spectrum. ^{1}H NMR (THF-d_8, −58 °C): δ 7.82 (d, 8.0, 1 H), 7.30 (d, 7.2, 1 H), 7.06 (m, 2 H), 7.15 (dd, 6.9, 7.2, 1 H), 1.60 (s, 3 H) (the CH_2 group of the metallacycle was obscured by phosphine resonances). ^{13}C{^{1}H} NMR (THF-d_8, −58 °C, assignments of CH_3, CH_2, CH, and C made from ^{13}C DEPT spectra) δ 164.41 (s, C), 129.07 (s, CH), 126.86 (d, 19.2, CH), 126.55 (s, CH), 125.46 (s, CH), 123.88 (s, CH), 93.12 (s, C), 40.88 (s, CH_3), 0.99 (dm, 49, CH_2). ^{31}P{^{1}H} NMR (THF-d_8, −26 °C) ABCD simulation, where B and C are assigned as the mutually trans PMe_3 ligands: δ_A 11.36, δ_B 0.46, δ_C −2.02, δ_D −12.12, $J_{AB} = 34.7$, $J_{AC} = 34.8$, $J_{AD} = 5.8$, $J_{BC} = 363.4$, $J_{BD} = 26.3$, $J_{CD} = 26.5$.

(8) We recently found that addition of the chelating phosphine 1,2-bis(dimethylphosphino)ethane (DMPE) to solutions of **3** cleanly formed the bis(DMPE) analogue, $(DMPE)_2Ru(\eta^2\text{-}OC(Me)(Ph)CH_2)$, which was isolated in pure form. Infrared and solution NMR data, as well as microanalysis, are consistent with this formulation.

(9) The alcohol was identified by comparison of the ^{1}H NMR spectrum and GC retention time with those of an authentic sample purchased from Aldrich.

(10) Complex **2** is also formed on addition of acetone to benzyne complex **1**. It was isolated in 28% yield in this reaction and fully characterized; details will be reported in a full paper.

(11) Identified by comparison of the ^{1}H NMR spectrum and GC retention time with those of an authentic sample purchased from Aldrich.

(12) Preliminary studies involving the addition of 3′-methylacetophenone and 4′-fluoroacetophenone yielded compounds different from those obtained by the addition of parent acetophenone, but containing the same overall spectral features. This indicates that the same type of reaction occurred with these substrates and that the aryl ring of the product is that of the added acetophenone.

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diphenylacetylene, or isobutylene did not significantly affect either the room-temperature ^{1}H or ^{31}P{^{1}H} NMR spectra of 3 or the thermolysis reaction to form the C–C cleaved product 2.

Although the intriguing potential intermediate $L_4Ru{=}O$ could be involved in some of these transformations, we believe it is more likely that the reactions are initiated by attack of electrophile at the nucleophilic oxygen of the metallacycle, followed by elimination of olefin (a process analogous to that observed in electrophile-catalyzed dehydration of tertiary alcohols).[14] Additional mechanistic studies on these unusual C–O and C–C cleavage reactions are in progress to test this hypothesis, as is further exploration of the chemistry of metallacycle 3.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Supplementary Material Available: Spectroscopic and analytical data for complexes 3–5 and 7–10 (3 pages). Ordering information is given on any current masthead page.

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Syntheses of a σ,π-Bidentate Bicyclo[3.2.1]octene Complex of Manganese via Carbene–Dienyl Coupling and of a Novel η^2-Arene Species

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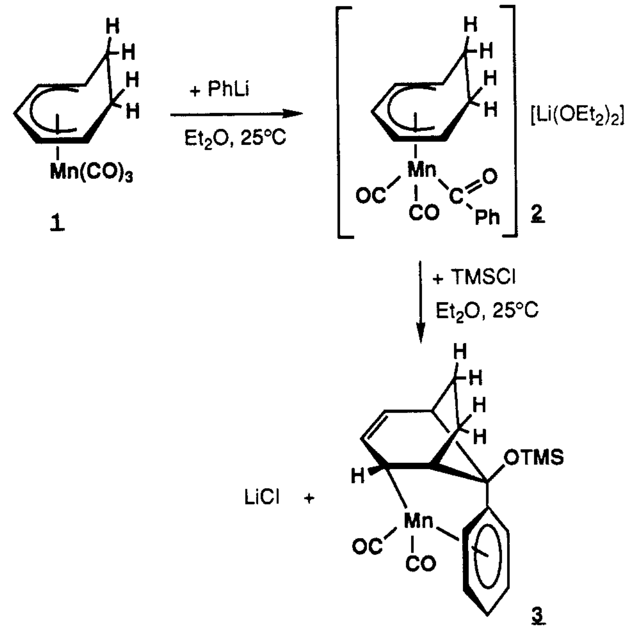
The syntheses, reactions, and study of transition-metal carbene complexes containing olefin and/or polyene ligands have attracted much interest in recent years,[1] particularly in their relevance to olefin metathesis catalysis,[2] cyclopropanation reactions,[3] and the Ziegler–Natta polymerization of olefins.[4] In contrast, the synthesis of dienyl or trienyl complexes containing carbene ligands has not been reported, due in part to a lack of suitable acylmetallate precursors.

In our laboratory we are attempting to develop new synthetic strategies that involve intramolecular acyl– and/or carbene–polyene coupling in dienyl–acyl and dienyl–carbene complexes. It is hoped that this approach will prove of synthetic use in both the stereoselective functionalization of polyenes and the construction of bicyclic rings.

Herein we describe the formation of a novel bidentate bicyclic ligand that appparently results from a coupling between a carbene ligand and the C(1) and C(5) carbons of a cycloheptadienyl ring. The product is a bicyclo[3.2.1]oct-2-ene complex (3) in which the organic moiety is both σ-bound to the metal and π-bound through an arene substituent at C(8). More interestingly, the reaction of this new complex with triphenylphosphine results in the formation of an (η^3-allyl)Mn(CO)$_2$(PPh$_3$) derivative which contains a highly distorted transition-metal–η^2-arene interaction. This latter crystallographically characterized complex shows the arene ligand as principally η^1-bonded to the metal with a Mn–C distance of 2.445 (10) Å.

Scheme I



Reaction of [Mn(CO)$_3$(η^5-C$_7$H$_9$)] (1)[5] with 1 equiv of PhLi in diethyl ether gives the highly air and moisture sensitive orange crystalline salt [Mn(CO)$_2$(C{O}Ph)(η^5-C$_7$H$_9$)][Li(Et$_2$O)$_2$] (2) (Scheme I), which has been spectroscopically characterized.[6] Reaction of 2 with TMSCl [TMS = Si(CH$_3$)$_3$] in diethyl ether at room temperature does not give the expected carbene complex but the new orange species (3) (Scheme I).

Complex 3 can be isolated in 84% yield (based on 1) as a moderately stable orange solid and was fully characterized by elemental analysis and ^{1}H, ^{13}C, ^{1}H–^{1}H (2D COSY), and ^{1}H–^{13}C (2D COSY) NMR and IR spectroscopy.[6] It appears to derive from the coupling of a "transient" carbene ligand with the terminal dienyl carbon atoms of the C$_7$ ring concomitant with migration of the metal to the phenyl group of the original acyl ligand. The formation of an η^6-arene complex was confirmed by the absence of any aromatic protons in the ^{1}H NMR spectrum of 3 and the presence of signals between δ 4.90 and 6.20 typical of π-bound arenes.[1c] As shown in Scheme I, the metal remains σ-bonded to the original C$_7$ ring at C(4), making the new ligand a σ,π-bidentate bicyclo[3.2.1]oct-2-ene[7] moiety.

The coupling of dienes with "transient" carbene ligands on iron has been reported by Chen and co-workers,[1] and in the reaction of [(η^4-cycloocta-1,5-diene)(CO)$_2$FeC{O}Ph]$^-$ with TMSCl, complete migration of iron to the phenyl group was observed without any residual σ-bonding to the original eight-membered ring.[1c] The formation of 3 differs in that it gives a bidentate ligand and most likely proceeds via sequential alkyl–carbene and alkyl–olefin migratory insertions, assuming the dienyl ligand is represented as a diene–alkyl species. A similar mechanism is proposed in ref 1c for the formation of the iron complex mentioned above.

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