

monitored by IR was complete after 36 h. The yellow solution was then evaporated to dryness under reduced pressure. The orange oil obtained was extracted with pentane (80 mL) in the presence of activated carbon (200 mg). Concentration of the filtrate and cooling to -78°C gave yellow microcrystals which were dried in vacuo and subsequently characterized as $\text{Ru}(\text{CO})_2(\eta^3\text{-C}_5\text{H}_5)_2$ (5; 130 mg, 34%). Traces of $\text{Ru}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_6)$ were detected in the mother liquor. Data for 5: mp 86°C ; IR (pentane) $2020, 1951\text{ cm}^{-1}$ (CO); MS (70 eV, ^{102}Ru), m/e (relative intensity) 318 (M^+ , 14), 290 (10), 262 (40), 260 (87), 208 (21), 180 (100), 102 (44); $^1\text{H NMR}$ (CDCl_3) δ 5.70 (dd, $J_{bc} = 6.0, J_{cd} = 6.5$ Hz, 2 H, H_c), 4.70 (ddd, $J_{dex} = 6.5, J_{bd} = 1.5$ Hz, 2 H, H_d), 3.49 (ddd, $J_{ab} = 7.0$ Hz, 2 H, H_b), 2.87 (ddd, $J_{gem} = 15.5, J_{enf} = 11, 7$ Hz, 2 H, H_{en}), 2.73 (dddd, $J_{exf} = 7.5, 1.3$ Hz, 2 H, H_{ex}), 2.58 (dd, $J_{af} = 5.5, <0.5$ Hz, 2 H, H_a), 1.38 (m, $J_{gem} \approx 13$ Hz, 4 H, $\text{H}_{fm}, \text{H}_{fx}$); $^{13}\text{C NMR}$ (CDCl_3) δ 203.6 (s, CO), 101.1 (d, $J_{CH} = 164$ Hz), 82.8 (d, $J_{CH} = 157$ Hz), 55.1 (d, $J_{CH} = 163$ Hz), 53.4 (d, $J_{CH} = 132$ Hz, C_a), 31.8 (t, $J_{CH} = 129$ Hz), 27.2 (t, $J_{CH} = 127$ Hz). Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Ru}$: C, 52.99; H, 5.08. Found: C, 53.22; H, 5.38.

Reaction of 3 with Borohydride. Complex 3 (110 mg, 0.29 mmol) was dissolved in CH_2Cl_2 (40 mL) and the solution cooled to -20°C . An excess of NaBH_4 (120 mg, 3.2 mmol) was added and the mixture stirred at -20°C for 1 h. The solvent was then evaporated under reduced pressure at -20°C , and the resulting solids were extracted with cold pentane (2×30 mL). The pentane solution was evaporated under reduced pressure at -20°C , yielding

1 (70 mg, 82%) as a yellow oil. No trace of 2 was detected. Under similar conditions with NaBD_4 , the formation of $\text{Ru}(\text{CO})(\eta^5\text{-C}_6\text{H}_6\text{D})(\eta^3\text{-C}_6\text{H}_9)$ (1D) was observed. The deuterium was assigned exo on the methylene of the cyclohexadienyl ring from the $^1\text{H NMR}$ (CDCl_3 , 250 K): 1D as for 1 except for δ 2.83 (t, $J_{cdn} = 6$ Hz, $J_{HD} < 1$ Hz, 1 H, H_{dn}) and no signal at δ 2.65.

Reaction of 4 with Borohydride. Complex 4 (135 mg, 0.36 mmol) was dissolved in CH_2Cl_2 (40 mL) and the solution cooled to -20°C . An excess of NaBH_4 (120 mg, 3.2 mmol) was added and the mixture stirred at -20°C for 1 h. The solvent was evaporated under reduced pressure at -20°C , and the resulting solids were extracted with cold pentane (2×30 mL). The pentane solution was evaporated under reduced pressure at -20°C , yielding 2 (75 mg, 72%) as a yellow oil. No trace of 1 was detected. The reaction was repeated at -50°C with similar results. With NaBD_4 the formation of $\text{Ru}(\text{CO})(\eta^4\text{-C}_6\text{H}_7\text{D})(\eta^4\text{-C}_6\text{H}_8)$ (2D) was observed. The deuterium was assigned exo on a methylene group from the $^1\text{H NMR}$: 2D as for 2 except for δ 1.85 (m, $J_{HD} \approx 1.7$ Hz, 4 H, H_{cn}) and 1.54 (dm, 3 H, H_{cx}).

Acknowledgment. We thank the Swiss National Science Foundation for generous financial support.

Registry No. 1, 103349-61-7; 1D, 103349-67-3; 2, 92468-32-1; 2D, 103349-68-4; 3, 103349-63-9; 4, 103349-65-1; 5, 103349-66-2; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1.

Dicarbonyl(η^5 -cyclopentadienyl)ruthenium Complexes of Cycloheptatrienyliene and Two Isomeric Benzocycloheptatrienylienes

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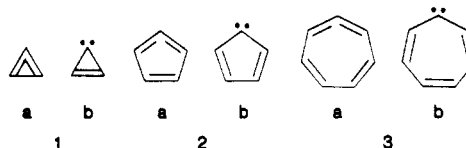
Received January 17, 1986

Dicarbonyl(1,3,5-cycloheptatrienyl)(η^5 -cyclopentadienyl)ruthenium [$(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2(\text{C}_7\text{H}_7)$] (13; as a mixture of isomers) and two benzannelated analogues, dicarbonyl(1,2-benzocycloheptatrien-5-yl)(η^5 -cyclopentadienyl)ruthenium (22) and dicarbonyl(1,2-benzocycloheptatrien-4-yl)(η^5 -cyclopentadienyl)ruthenium (19), have been prepared by reaction of the corresponding cycloheptatrienyllithiums with RpBr ($\text{Rp} = \text{dicarbonyl}(\eta^5\text{-cyclopentadienyl})\text{ruthenium}$). Hydride abstraction from these σ complexes with triphenylcarbenium hexafluorophosphate gave the corresponding carbene complexes 15, 20, and 19, respectively. In all cases the salts behaved like their iron analogues in that they exhibited properties of carbene σ complexes (e.g., 15b) rather than allene π complexes (e.g., 15a). Substitution of tributylphosphine for carbonyl on the parent 15 did not change this structural preference. The barrier to rotation about the carbon-metal bond in the phosphine-substituted carbene complex 29 was found to be 8.5 kcal/mol which is 1.1 kcal/mol less than that of the corresponding iron complex. Attempts to prepare $\text{C}_7\text{H}_7\text{COCO}(\text{CO})_4$ (as a potential precursor to a cobalt analogue of the cycloheptatrienyliene complex 15) by reaction of $\text{Co}(\text{CO})_4^-$ with $\text{C}_7\text{H}_7\text{COCl}$ failed; the only isolated product was the cycloheptatrienyl cluster compound 11.

Introduction

Strained organic molecules¹ have received extensive attention over the past several decades. Of these, one of the more unusual subgroups includes the strained cyclic, conjugated allenes 1a, 2a, and 3a which have as their re-

spective valence isomers, carbenes 1b, 2b, and 3b. To date

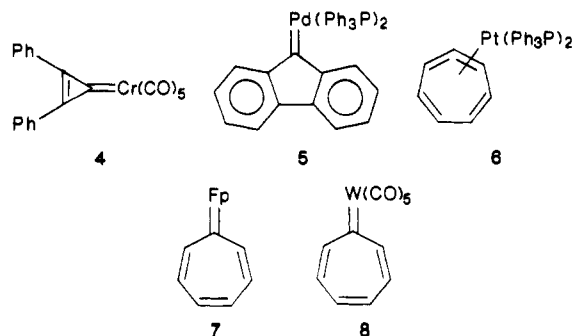


the attention that has been devoted to the question of structural preference in these isomeric pairs has varied from none to rather extensive. For instance, although there can be little question but that the lowest energy form of

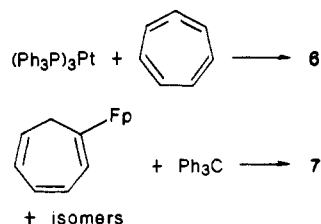
(1) Cf. Greenberg, A.; Liebman, J. F. *Strained Organic Compounds*; Academic Press: New York, 1978. March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; pp 130-140. Carey, F. A.; Sundberg *Advanced Organic Chemistry*; 2nd ed.; Plenum: New York, 1985; pp 141-144 and references therein.

1 is the carbene,² to our knowledge and for obvious reasons 1a has never even been considered as a possible alternative. Similarly, 2 is typically assumed to be a carbene, and there is no question but that its ground state is the triplet carbene.⁴ However, although the viability of 2a has recently been addressed,⁴ to our knowledge its energy relative to singlet 2b has not been resolved. In marked contrast to 1 and 2, the two forms of 3 have been studied both theoretically⁵⁻⁷ and experimentally⁸ in considerable detail, and it is generally conceded that the ground state is the allene form 3a. In this case the unresolved question is the viability of 3b as a reactive intermediate because while some of the chemistry of 3 is that expected of a carbene,^{8,9} one calculation⁷ has concluded that 3b is, in fact, simply a transition state for the interconversion of enantiomeric allenes.

Transition-metal complexes of derivatives of both 1 and 2 have been prepared, and in all cases they exist exclusively in the "carbene" forms (e.g., 4¹⁰ and 5¹¹). In contrast, the



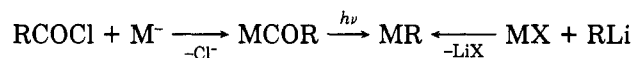
structures of complexes of 3 appear to depend on the metal moiety; the $(\text{Ph}_3\text{P})_2\text{Pt}$ complex¹² has the allene structure 6 while the Fp^+ ($\text{Fp} = \text{dicarbonyl}(\eta^5\text{-cyclopentadienyl})\text{iron}$) and $(\text{CO})_5\text{W}$ complexes¹³ have structures 7 and 8. Significantly, in all three cases the observed isomeric form is the same as that expected of the synthetic method used to prepare it. Thus, 6 was prepared by trapping cycloheptatetraene with $(\text{Ph}_3\text{P})_3\text{Pt}$, and both 7 (and some of its



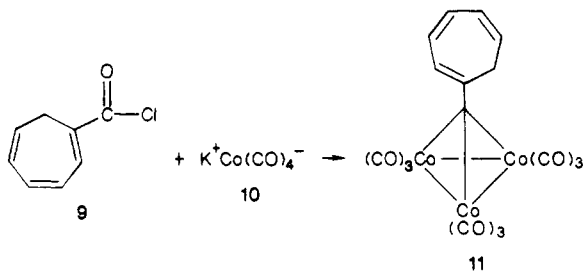
derivatives) and 8 were prepared by hydride abstraction from appropriate σ complexes. Furthermore, in no case have we found any evidence for conversion of any of the complexes to other isomeric forms; e.g., 6 is not fluxional¹² to 80 °C, and neither 7 nor 8 has ever shown any tendency to isomerize to a more stable allene form.¹⁴ Thus, although it is likely that 6, 7, and 8 are all the lowest energy isomers, there is no evidence to date that precludes any or all being initially formed as the higher energy isomer for which activation barriers are high enough to prevent conversion to ground-state forms before thermal decomposition. As the isomerization of one form to the other should be a viable process, we have undertaken the preparation of other organo-transition-metal complexes with the C_7H_6 moiety. In this paper, we report our unsuccessful attempts to prepare the $(\text{CO})_4\text{Co}$ derivative, and our successful preparation of a series of Ru derivatives which, once again, did not exhibit the aforementioned isomerization.

Results and Discussion

Two general methods are available for the preparation of potential σ complex precursors to the C_7H_6 -bound target molecules: the method of King and Bisnette¹⁵ employing a metal anion and an acid chloride with subsequent decarbonylation to give the σ complex and treatment of a metal halide with an alkyllithium to give the σ complex directly.



As we had experienced success using the metal anion/acid chloride/decarbonylation approach in the preparation of cyclopropyl and cycloheptatrienyl σ complexes of dicarbonyl(η^5 -cyclopentadienyl)iron (Fp),¹⁶ as our first approach we elected to use the same strategy for tetracarbonylcobalt and dicarbonyl(η^5 -cyclopentadienyl)ruthenium complexes of 3. Unfortunately, this strategy failed for both metals. In the cobalt case, reaction of $\text{KCo}(\text{CO})_4$ (10) with $\text{C}_7\text{H}_7\text{COCl}$ (9) gave only the cobalt cluster 11,¹⁷



(2) Lee, T. J.; Bunge, A.; Schaefer, H. F. III *J. Am. Chem. Soc.* **1985**, *107*, 137.

(3) Wasserman, E.; Barash, L.; Trozzolo, A. M.; Murray, R. W.; Yager, W. A. *J. Am. Chem. Soc.* **1964**, *86*, 2304.

(4) Johnson⁶ has addressed the question of the viability of 2a and has found that, although MNDO places it 21.2 kcal/mol above the triplet ground state, it does represent a shallow energy minimum and may be involved in singlet reactions of cyclopentadienylidene.

(5) Johnson, R. P. In *Molecular Structures and Energetics*; Libman, J. F., Greenberg, A., Eds.; Verlag Chemie: Weinheim, Germany, 1900; Vol. 3. Johnson, R. P., University of Vermont, private communication.

(6) Radom, L.; Schaefer, H. F. III; Vincent, M. A. *Nouv. J. Chim.* **1980**, *4*, 411. Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 6179. Tyner, R. L.; Jones, W. M.; Ohrn, Y.; Sabin, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 3765.

(7) Waali, E. E. *J. Am. Chem. Soc.* **1981**, *103*, 3604.

(8) Kirmse, W.; Loosen, K.; Sluma, H. D. *J. Am. Chem. Soc.* **1981**, *103*, 5935. West, P. R.; Chapman, O. L.; LeRoux, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 1779. Harris, J. W.; Jones, W. M. *J. Am. Chem. Soc.* **1982**, *104*, 7329 and references therein.

(9) It must be emphasized that there has appeared unequivocal evidence for only the allene form 3a, and, in fact, one theoretical study⁷ has concluded that the carbene form does not even represent an energy minimum; it is predicted to be the transition state for the interconversion of enantiomeric allenes.

(10) Ofele, K. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 950. Ofele, K. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 916. Gompfer, R.; Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 456. Weiss, R.; Preisner, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 457. Kawada, Y.; Jones, W. M. *J. Organomet. Chem.* **1980**, *192*, 87.

(11) Nakamura, A. *Justus Liebigs Ann. Chem.* **1975**, 626. Herrmann, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 777.

(12) Winchester, W. R.; Jones, W. M. *Organometallics* **1985**, *4*, 2228.

(13) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 2458. Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *Inorg. Chem.* **1982**, *21*, 1321. Allison, N. T.; Kawada, Y.; Jones, W. M. *J. Am. Chem. Soc.* **1978**, *100*, 5224.

(14) Equilibration of 7 or 8 with a higher energy allene isomer would be difficult to detect. In contrast, it should be relatively straightforward to monitor equilibration of ground-state allene isomers, which are chiral with achiral carbene isomers.

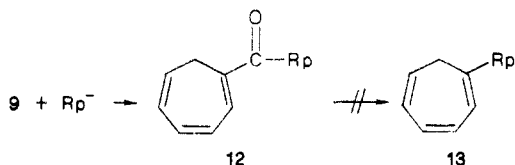
(15) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15.

(16) Manganiello, F. J.; Christensen, L. W.; Jones, W. M. *J. Organomet. Chem.* **1982**, *235*, 327-334. Jones, W. M., unpublished results.

(17) While formation of the cluster was surprising, it is not without precedent: Bartl, Boese, and Schmid¹⁸ found that reaction of the same salt with 2,4,6-trimethylbenzoyl chloride gave an analogous cluster in correspondingly low yield.

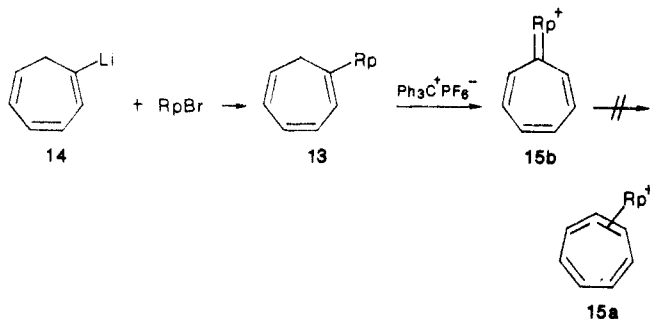
(18) Bartl, K.; Boese, R.; Schmid, G. *J. Organomet. Chem.* **1981**, *206*, 331.

none of the desired acyl complex was detected. With ruthenium, reaction of Na^+Rp^- ($\text{Rp} = \text{dicarbonyl}(\eta^5\text{-cyclopentadienyl})\text{ruthenium}$), prepared by reduction of RpBr with sodium amalgam,¹⁹ with the acid chloride **9** gave **12** in 64% yield as an air-sensitive yellow, crystalline solid.



Unfortunately, all attempts to induce decarbonylation to **13** failed. The photostability of **12** was surprising as, under similar conditions, the analogous iron compound decarbonylated smoothly to give the corresponding σ complex in good yield.¹⁶ Extended photolysis resulted in rather marked changes in the cycloheptatrienyl ring resonances (as monitored by ^1H NMR). As a result, this approach for preparing **13** was abandoned.

In view of these results, we turned our attention to the alternate route developed by Allison:¹³ reaction of the mixture of alkenyllithiums represented by **14**²³ with RpBr . Under conditions similar to those used for preparation of the iron analogue, the σ complex **13** (mixture of isomers)²³ was isolated in 38% yield as an air-sensitive, yellow oil. Treatment of this mixture with triphenylcarbenium hexafluorophosphate gave **15** quantitatively. Assignment of



the carbene structure **15b** rather than the allene **15a** is based primarily on ^1H and ^{13}C NMR. In **15b** the hydrogens bound to the carbons adjacent to the carbene carbon are equivalent and, by analogy with the Fp^+ analogue,¹³ should appear at relatively low field. In fact, they appear as a doublet at δ 9.50. In contrast, the same hydrogens in **15a** are nonequivalent and should appear at considerably higher field (no Rp^+ allene models are known but the Fp^+ complex of 1,2-cycloheptadiene, at -20°C , shows resonances at δ 4.45 and 6.55 for the complexed and the non-complexed hydrogens respectively).²⁴ Further, if the proximal hydrogens appeared to be equivalent due to fluxionality, the averaged resonances should appear at about 5 ppm, some 4.5 ppm upfield from the observed. Additional evidence for the carbene structure was found in the chemical shift of the carbene carbon in the ^{13}C

(19) This was found to be preferable to reduction of Rp_2 because, whereas relatively pure RpBr could be quite readily prepared in large amounts by the method of Efraty et al.,²⁰ in our hands literature methods for preparation of Rp_2 ²¹ did not give either the reported yield or purity.

(20) Eisenstadt, A.; Tannenbaum, R.; Efraty, A. *J. Organomet. Chem.* 1981, 227, 317.

(21) Though RpH was formed in situ as reported,²² in our hands the oxygen-promoted coupling of the ruthenium centers resulted in low yields of impure product.

(22) Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* 1975, 1710.

(23) **14** is a mixture of 1,2- and 3-isomers, and except where noted, the same is the case for σ complexes such as **13**.

(24) Manganiello, F. J.; Oon, S. M.; Radcliffe, M. D.; Jones, W. M. *Organometallics* 1985, 4, 1069-1072.

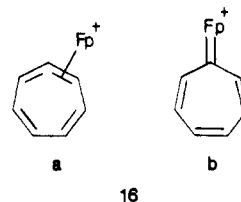
Table I. ^{13}C NMR Carbene Carbon Resonances (Fe vs. Ru)

type	Fe	Ru
	242.3 ¹³	223.6
	265.9 ¹³	244.7
	201.0 ¹³	186.6
	278.8 ³⁰	256.2

^a $\text{Mpp} = \text{carbonyl}(\eta^5\text{-cyclopentadienyl})(\text{tri-}n\text{-butylphosphine})\text{-metal}$.

NMR. If **15** has the allene structure, the resonance of the central carbon would be expected to be considerably upfield (δ 150.1 for the Fp^+ complex of 1,2-cycloheptadiene²⁴) from the observed δ 223.6. On the other hand, the observed resonance is completely consistent with structure **15b** in that it is slightly upfield from the corresponding resonance of the Fp^+ analogue¹³ (δ 242.3²⁵) which an X-ray structure determination has confirmed the carbene form. The upfield shift upon going from iron to ruthenium was found to be general for all complexes prepared in this work (Table I) and is not surprising since a similar shift has been observed in the Cr, Mo, W triad ($(\text{CO})_5\text{M}=\text{CPh}_2$, $\text{M} = \text{Cr}$, Mo , W ; δ 399.4,²⁷ 384.2,²⁸ and 358.3,²⁹ respectively). Finally, the overall similarity between the ^1H NMR spectra of **15** and the Fp^+ analogue is striking.

The influence of benzannelation on equilibria between the two forms of **3** has been studied by INDO MO calculations³¹ with the conclusion that benzannelation as in **17** substantially increases the separation between the two forms (as compared with **3a** and **3b**) while benzannelation as in **18** reduces it. Furthermore, EHMO calculations predict that whereas **3a** is the ground state for the free ligand, **16b** is the ground state for the corresponding Fp^+ complex.³² On the assumption that benzannelation would



have, at least qualitatively, a similar effect on transition-

(25) The ^{13}C chemical shift of the carbene carbon in cycloheptatrienyldiene complexes invariably appears at much higher field than most transition-metal carbene complexes. This is not surprising since incorporation of the carbene carbon into a tropylium ring should increase the separation between the σ bond HOMO and the carbene carbon LUMO as well as delocalize the LUMO into the ring, both of which would reduce the paramagnetic contribution to the chemical shift.²⁶

(26) Fenske, R. F. In *Organometallic Compounds: Synthesis, Structure and Theory*; Shapiro, B. L., Ed.; Texas A&M University: College Station, TX, 1983.

(27) Fischer, E. O.; Held, W.; Kriessl, F. R.; Frank, A.; Huttner, G. *Chem. Ber.* 1977, 110, 656.

(28) Beatty, R. P.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* 1981, 103, 238.

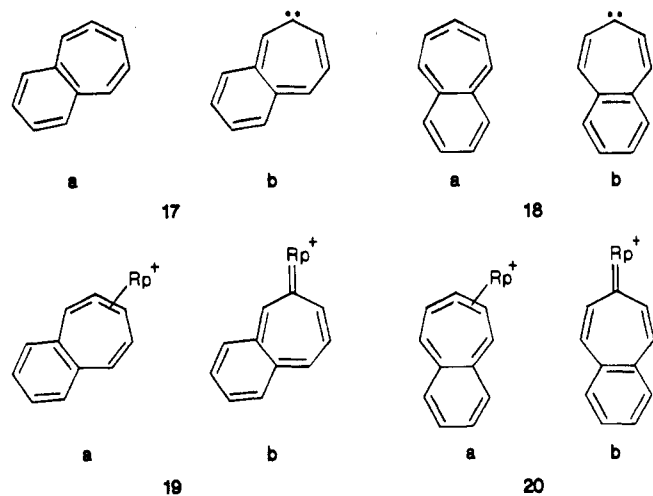
(29) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* 1977, 99, 2127.

(30) Manganiello, F. J.; Radcliffe, M. C.; Jones, W. M. *J. Organomet. Chem.* 1982, 228, 273.

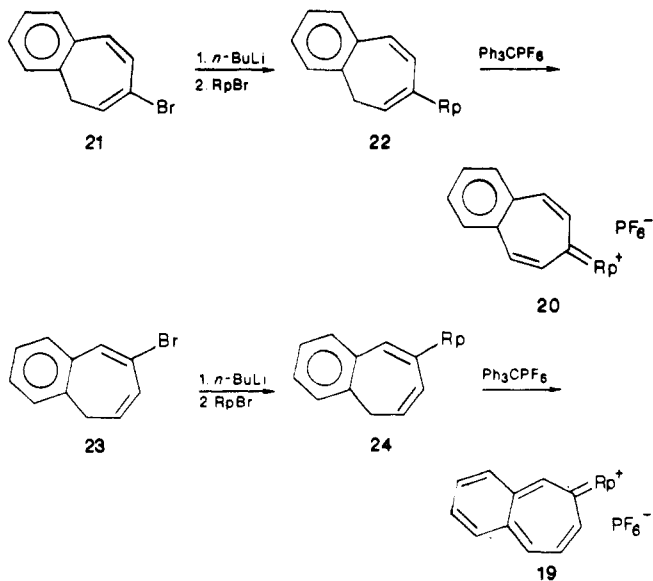
(31) Balci, M.; Winchester, W. R.; Jones, W. M. *J. Org. Chem.* 1982, 47, 5180.

(32) Unpublished results of W. R. Winchester, University of Florida.

metal complexes and the free ligands, we can predict that either the energy gap separating 19a from 19b should be reduced or, possibly, the ground states could change with the allene complex now becoming the preferred form. Although this was not found to be the case with the Fp^+ (Fp = dicarbonyl(η^5 -cyclopentadienyl)iron) of 17,¹³ we thought it would be interesting to see if a change to ruthenium might lead to a different structural preference. We therefore undertook to prepare 19. To complete the series we also prepared 20. In each case the required σ

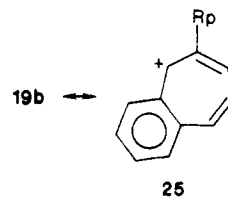


complex was prepared by reaction of the appropriate alkenyllithium with RpBr as illustrated below. As was



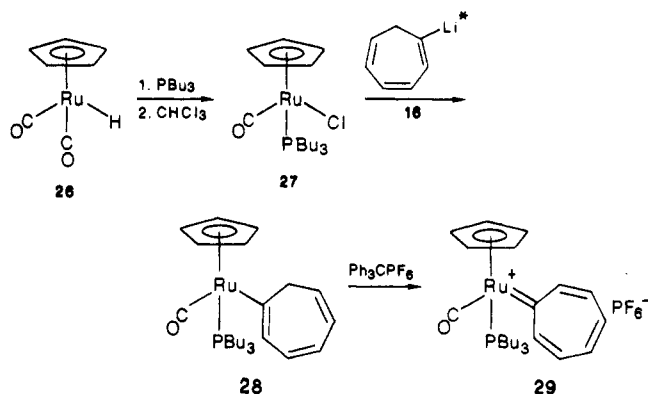
found with the corresponding Fp complex,¹³ treatment of 22 with triphenylcarbenium hexafluorophosphate gave a salt with properties expected of 20b (equivalent hydrogens proximal to the carbene carbon with a chemical shift of δ 9.70 and a low-field central carbon resonance at δ 244.7). The result of hydride abstraction from 24 was also found to be analogous to the corresponding Fp system.¹³ Thus, even though the product could not be obtained analytically pure, from the ^1H and ^{13}C NMR spectra, there is little question but that 19 was formed and that it has structure 19b rather than 19a. Thus, in the ^1H spectrum, there is a singlet at δ 10.17 (one of the hydrogens proximal to the carbene carbon) and a doublet at δ 9.70 (the other proximal hydrogen), and the ^{13}C spectrum shows a resonance at δ 186.63. As above, all of these observations point to structure 19b with a high contribution from resonance forms such as 25 which is believed to be the reason the

proximal hydrogens are at rather low field while the carbene carbon is shifted to high field (low LUMO coefficient on the carbene carbon²⁶) relative to, for example, 20.



In a cationic complex of 3, it would be expected that more positive charge would reside on the metal in the allene form than in the tropylium ion form. Substitution of a phosphine ligand for a carbonyl should therefore favor the allene relative to the carbene. We therefore prepared the tri-*n*-butylphosphine-substituted σ complex 28 as follows.

Addition of *n*- Bu_3P to a preformed solution of the metal hydride 26 gave $\text{Cp}(\text{CO})(n\text{-Bu}_3\text{P})\text{RuH}$. Addition of CHCl_3 resulted in quantitative formation of the phosphinylated halide 27.³³ Addition of this halide to a solution containing a mixture of 1-, 2- and 3-cycloheptatrienyllithium gave the desired σ complex 28 (only the 1-isomer).³⁴ Treatment of 28 with $\text{Ph}_3\text{C}^+\text{BF}_4^-$ gave, once again, a salt that showed only the properties expected of the carbene form 29.



With the phosphine-substituted carbene complex in hand, we thought it would be interesting to compare the barrier to rotation about the C-M bond with the corresponding iron complex. In the latter case we were able to show that the barrier had a back-bonding electronic as well as (presumably) a steric component.³⁰ In the ruthenium case in which back-bonding should be more favorable, the electronic component should increase and thus retard rotation. On the other hand, the C-M bond should be longer, and this should reduce steric resistance to rotation.

The barrier was determined by variable-temperature NMR, and the resulting spectra are shown in Figures 1 and 2. From these spectra the free energy of activation for rotation about the C-M bond was determined by the following equation³⁵ to be 8.5 kcal/mol.

$$\Delta G^* = RT_c(\ln T_c/\Delta\nu + 22.96)$$

This is somewhat less than the barrier for the iron analogue (9.6 kcal/mol) which leads us to conclude that, upon going from iron to ruthenium reduction in steric constraint must

(33) Rowan, A. J.; Howell, J. A. S. *J. Chem. Soc., Dalton Trans.* 1980, 1845.

(34) Formation of only one of the three possible isomers is unusual but not unique; the same was observed in the preparation of the precursor to $(\text{CO})_5\text{WC}_7\text{H}_6$.

(35) Jackman, L. M.; Cotton, F. A. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1975; p 64.

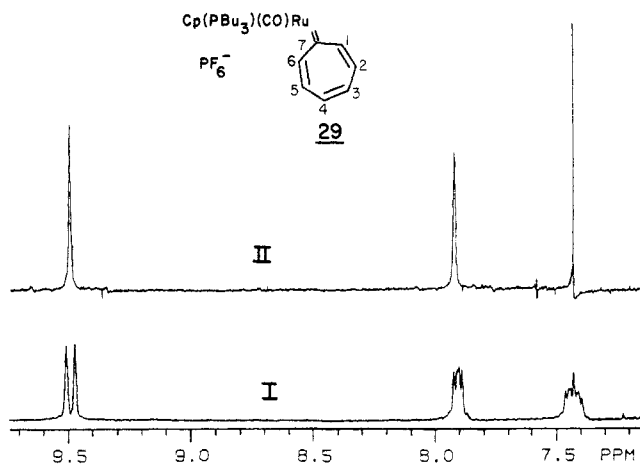


Figure 1. (I) 300-MHz ^1H NMR spectrum of compound 29. (II) 300-MHz ^1H NMR spectrum of compound 29 with Irradiation of $\text{H}_{2,5}$.

be more important than increased back-bonding.

Experimental Section

Benzene, diethyl ether, hexane, and tetrahydrofuran were distilled from sodium benzophenone ketyl. Methylene chloride was distilled from P_2O_5 after 24-h reflux. Silica gel was either Baker 60–200 mesh or M.C.B. 230–400 mesh. The latter was used for low-pressure chromatography according to the method of Still et al.³⁶ Alumina was Brockman 80–200 mesh activity I which was deactivated to activity II by the addition of H_2O (3% w/w). Both silica gel and alumina was degassed overnight (0.25 mmHg, 25 °C) prior to use. NMR spectra were taken on a JEOL PMX-60 (60 MHz), JEOL FX-100 (100 MHz), or a Nicolet NT-300 (300 MHz). Infrared data were recorded on a Perkin-Elmer 137 spectrophotometer. Atlantic Microlab, Inc. performed C, H analyses. Melting points (uncorrected) were obtained by using a Thomas-Hoover apparatus. All solutions containing transition metals or organolithium reagents, as well as any resulting solids, were manipulated under inert atmosphere (Schlenk tube or glovebox) conditions. $\text{Co}_2(\text{CO})_8$ and $\text{Ru}_3(\text{CO})_{12}$ were purchased from Strem Chemical Co. Compounds 10,³⁷ RpBr ,²⁰ 21,³⁸ and 23¹³ were prepared by literature methods.

Preparation of (1,3,5-Cycloheptatrien-1-yl)(μ_3 -methinyl)tricobalt Nonacarbonyl (11). Potassium tetracarbonylcobaltate (2.45 g, 11.68 mmol) was dissolved in 15 mL of THF and warmed to 40 °C with stirring. To this heated solution was added 1,3,5-cycloheptatriene-1-carbonyl chloride (9) (1.50 g, 9.70 mmol) in 10 mL of THF via syringe. Evolution of gas was apparent at the conclusion of addition and continued for several minutes. Upon cessation of gas evolution, alumina (neutral grade II, 5.0 g) was added, and the solvent was removed in vacuo. The resulting brown solid was placed 1 in. \times 6 in. column (alumina, neutral grade II) and eluted with pentane. A red-violet band eluting with the solvent front was collected and upon removal of solvent gave 0.100 g (6.5%) purple crystals: mp 72.0–72.5 °C; IR (pentane) ν_{CO} 2100 (s), 2050 (vs), 2040 (vs), 2020 cm^{-1} (s); ^1H NMR (CDCl_3) δ 2.90 (d, 2 H, $^3J_{\text{HH}} = 12$ Hz), 5.5–6.0 (1 H), 6.1–6.4 (m, 1 H), 6.5–6.8 (m, 3 H); ^{13}C NMR (CDCl_3) δ 38.50 (C_7), 122.42, 124.71, 127.88, 129.92, 131.09 (C_{2-6}), 154.58 (C_1), 199.81 ($\text{C}=\text{O}$), 280.00 ($\mu\text{-C}$); mass spectrum, m/e 532 (M^+), 504 ($\text{M}^+ - \text{CO}$), 476 ($\text{M}^+ - 2\text{CO}$), 448 ($\text{M}^+ - 3\text{CO}$), 420 ($\text{M}^+ - 4\text{CO}$), 392 ($\text{M}^+ - 5\text{CO}$), 364 ($\text{M}^+ - 6\text{CO}$), 336 ($\text{M}^+ - 7\text{CO}$), 308 ($\text{M}^+ - 8\text{CO}$), 280 ($\text{M}^+ - 9\text{CO}$), 103 (C_8H_7), 91 (C_7H_7). Anal. Calcd for $\text{C}_{17}\text{H}_7\text{O}_9\text{Co}_3$: C, 38.38; H, 1.33. Found: C, 38.27; H, 1.39.

Preparation of Dicarbonyl(1,3,5-cycloheptatriene-1-carbonyl)(η^5 -cyclopentadienyl)ruthenium (12). Bromodicarbonyl(η^5 -cyclopentadienyl)ruthenium (0.500 g, 1.65 mmol) was

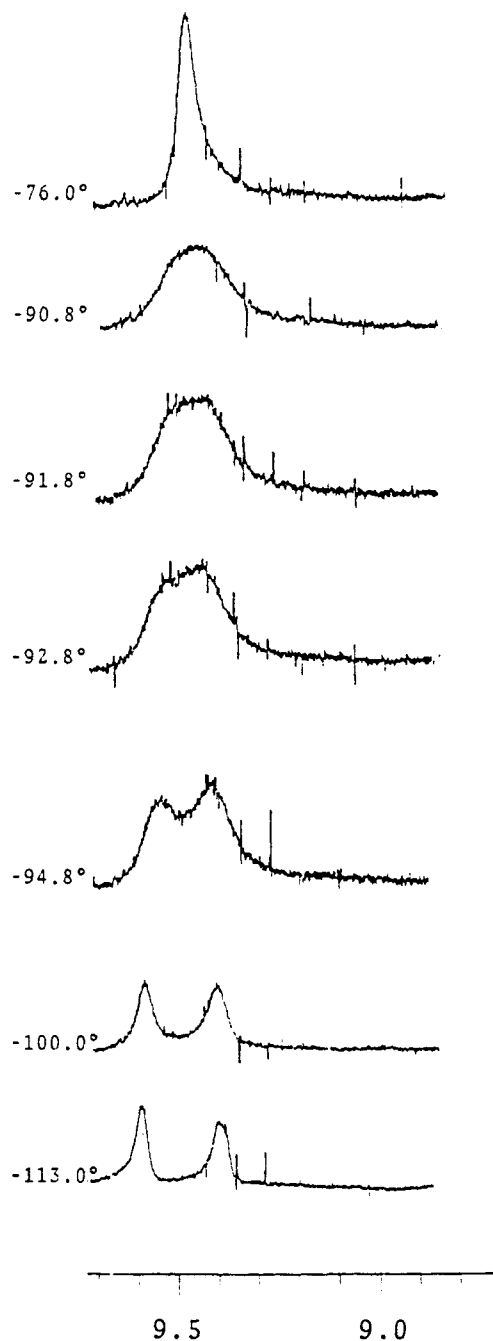


Figure 2. 300-MHz ^1H NMR spectrum of compound 29 (in CD_3COCD_3) with irradiation of $\text{H}_{2,5}$ for determination of temperature of coalescence.

added as a yellow solid to a stirred sodium amalgam (0.250 g of Na, 10.9 mmol; 101.25 g of Hg, 0.505 mol) in 15 mL of THF at room temperature. The yellow solid gave rise to a green suspension immediately, which was allowed to stir for six hours at room temperature. The green suspension had become orange-red by this time and was separated from residual sodium amalgam via cannula into another Schlenk tube and cooled to -78 °C with stirring. To the solution of sodium dicarbonyl(η^5 -cyclopentadienyl)ruthenate at -78 °C was added 1,3,5-cycloheptatriene-1-carbonyl chloride (0.256 g, 1.65 mmol) in 10 mL of THF. The stirred solution was then allowed to warm to room temperature and stir over a 12-h period. Solvent was removed in vacuo, and the viscous orange-brown oil was extracted with benzene (3×30 mL). After filtration of the benzene extracts through a Celite mat (~ 20 g) on a coarse, sintered-glass frit, silica gel (1.0 g, 60–200 mesh) was added and solvent was removed in vacuo. The resulting orange solid was then placed on a 1 in. \times 9 in. silica gel column (230–400 mesh) and eluted with ethyl acetate–pentane (15% v/v) at 2 in./min. A yellow band was collected which upon removal of solvent in vacuo proved to be

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a viscous orange oil. After storage under vacuum (0.100 torr, 25 °C, 12 h), the oil crystallized to give 0.364 g (64%) of yellow crystals (12): IR (CDCl₃) ν_{CO} 2020 (vs), 1940 (vs), 1800 cm⁻¹ (w); ¹H NMR (100 MHz, CDCl₃) δ 2.4 (d, 2 H, ³J_{HH} = 7.1 Hz), 5.3 (s, 5 H), 5.3–5.4 (m, 1 H), 5.5–5.6 (m, 1 H), 6.7–6.8 (m, 3 H); ¹³C NMR (25 MHz, CDCl₃) δ 27.44 (C₇), 88.84 (Cp), 124.46, 126.61, 128.70, 132.79, 133.29 (C_{2-e}), 144.88 (C₁), 199.37 (C=O), 235.87 (C=O); mass spectrum, *m/e* 342 (M⁺), 314 (M⁺ - CO), 286 (M⁺ - 2CO), 91 (C₇H₇). Anal. Calcd for C₁₅H₁₂O₃Ru: C, 52.78; H, 3.54. Found: C, 52.64; H, 3.57.

Preparation of Dicarbonyl(1,3,5-cycloheptatrien-1-yl)(η^5 -cyclopentadienyl)ruthenium (13). A mixture of 1-, 2-, and 3-bromocycloheptatrienes³⁹ (0.570 g, 3.31 mmol) was dissolved in THF (10 mL) and cooled to -78 °C with stirring. *n*-Butyllithium (2.21 mL, 1.5 M solution in hexane) was added dropwise slowly, resulting in formation of the green-black color of the cycloheptatrienyllithiums. The solution was allowed to stir for 30 min at -78 °C. Bromodicarbonyl(η^5 -cyclopentadienyl)ruthenium (1.00 g, 3.31 mmol) was dissolved in THF (10 mL), cooled to -78 °C, and then added slowly to the cold (-78 °C) cycloheptatrienyllithium solution. The reaction vessel was allowed to warm to room temperature slowly and then stir for an additional 30 min. Silica gel (2.0 g, 60–200 mesh) was added to the solution and solvent removed in vacuo. The resulting orange solid was placed on a 1 in. \times 9 in. silica gel column (230–400 mesh) and eluted at 2.0 in./min with ethyl acetate-pentane (5% v/v). A yellow band was collected, and, upon removal of solvent in vacuo, 0.390 g (38%) of air-sensitive orange oil (13) was obtained: IR (neat) ν_{CO} 2015 (s), 1970 cm⁻¹ (vs); ¹H NMR (100 MHz, CDCl₃) δ 2.10 (t, 2 H, ³J_{HH} = 6.7 Hz), 2.60 (d, 2 H, ³J_{HH} = 6.5 Hz), 5.10 (s, 5 H), 5.20 (s, 5 H), 4.8–5.6 (m, 2 H each isomer), 5.8–6.8 (m, 3 H each isomer); ¹³C NMR (25 MHz, CDCl₃) δ 49.03 (C₇), 87.18 (Cp), 116.28, 125.39, 125.83, 132.07, 137.33, 141.52 (C₁–C₆), 200.29 (C=O), other isomer δ 27.73 (C₇), 88.50 (Cp), 113.60, 118.52, 126.85, 135.67, 141.18, 141.33 (C₁–C₆), 200.63 (C=O); mass spectrum, *m/e* 314 (M⁺), 286 (M⁺ - CO), 258 (M⁺ - 2CO). Anal. Calcd for C₁₄H₁₂O₂Ru: C, 53.67; H, 3.86. Found: C, 53.48; H, 3.91.

Preparation of Dicarbonyl(η^1 -cycloheptatrienyldiene)(η^5 -cyclopentadienyl)ruthenium Hexafluorophosphate (15). The σ complex 13 (0.235 g, 0.75 mmol) was dissolved in methylene chloride (7.0 mL) and cooled to -78 °C with stirring. Triphenylcarbenium hexafluorophosphate (0.291 g, 0.75 mmol) was dissolved in methylene chloride, cooled to -78 °C, and then added to the cold (-78 °C) solution of σ complex. The solution was allowed to stir for 30 min at -78 °C and slowly warm to room temperature with an additional 30 min of stirring. Solvent was removed until 2.0–3.0 mL remained, at which time the solution was cooled to -78 °C and diethyl ether (20 mL) was added, precipitating a brown solid. Filtration, washing (diethyl ether, 3 \times 15 mL), and subsequent vacuum drying (25 °C, 0.200 torr) resulted in 0.220 g (64%) of air-stable, brown solid 15: mp 180–181 °C; IR (CDCl₃) ν_{CO} 2020 (s), 1980 cm⁻¹ (vs); ¹H NMR (100 MHz, CD₃NO₂) δ 5.60 (s, 5 H), 7.90–8.35 (m, 2 H), 8.40–8.70 (m, 2 H), 9.50 (d, 2 H, ³J_{HH} = 10.0 Hz); ¹³C NMR (25.2 MHz, CD₃NO₂) δ 91.15 (Cp), 140.91 (C_{3,6}), 149.19 (C_{4,5}), 170.05 (C_{2,7}), 198.66 (C=O), 223.56 (C₁). Anal. Calcd for C₁₄H₁₁O₂F₆PRu: C, 36.77; H, 2.42. Found: C, 36.90; H, 2.48.

Preparation of Dicarbonyl(1,2-benzocycloheptatrien-5-yl)(η^5 -cyclopentadienyl)ruthenium (22). 1,2-Benzo-5-bromocycloheptatriene (21) (0.534 g, 2.42 mmol) was dissolved in 10 mL of THF and cooled to -78 °C with stirring. Butyllithium (1.0 mL 2.5 M solution, 2.5 mmol) was added slowly over a 3-min period, giving a blue-green solution, which was allowed to stir at -78 °C for 30 min. A cold (-78 °C) solution of R_pBr (0.730 g, 2.42 mmol) in 10 mL of THF was then added over a 10-min period, and upon completion of addition, the reaction mixture was allowed to stir for 60 min at -78 °C and 60 min at 25 °C. Solvent was then removed in vacuo and the residue taken up in benzene (3 \times 10 mL) and filtered through a Celite mat on a coarse, sintered-glass frit. To the filtered solution was added silica gel (5.0 g, 60–200 mesh), and the solvent was then removed in vacuo. The solid residue was then placed on a low-pressure, silica gel column (0.75 in. \times 9 in., 230–400 mesh prepared with ethyl acetate-

pentane, 1% v/v). Elution with ethyl acetate-pentane (1% v/v) brought down a pale yellow band with the solvent front; collection was begun when the band was 2 in. from the bottom of the column. Removal of solvent in vacuo and crystallization of the resulting pale yellow oil from CH₂Cl₂-hexane gave 0.120 g (14%) of pale yellow crystals (22): mp 105–106 °C dec; IR (CDCl₃) 2020 (s), 1960 cm⁻¹ (vs); ¹H NMR (100 MHz, CDCl₃) δ 2.95 (d, 2 H, ³J_{HH} = 6.7 Hz), 5.08 (s, 5 H), 5.59 (t, 1 H, ³J_{HH} = 6.7 Hz), 6.59 (s, 2 H), 7.10–7.33 (m, 4 H); ¹³C NMR (25 MHz, CDCl₃) δ 39.91 (C₇), 88.84 (Cp), 124.13, 124.71, 126.57, 127.39, 127.64, 133.24, 135.92, 137.87, 144.26 (10 vinyl and aromatic carbons), 200.84 (C=O); mass spectrum, *m/e* 364 (M⁺), 336 (M⁺ - CO), 308 (M⁺ - 2CO). Anal. Calcd for C₁₈H₁₄O₂Ru: C, 59.50; H, 3.88. Found: C, 59.43; H, 3.94.

Preparation of Dicarbonyl(η^1 -4,5-benzocycloheptatrienyldiene)(η^5 -cyclopentadienyl)ruthenium Hexafluorophosphate (20). The σ complex 22 (0.112 g, 0.308 mmol) was dissolved in methylene chloride (10 mL) and cooled to -78 °C. Triphenylcarbenium hexafluorophosphate (0.120 g, 0.308 mmol) was dissolved in methylene chloride (10 mL), cooled to -78 °C, and then added via cannula to the rapidly stirred solution of σ complex 22 at -78 °C, which darkened immediately from a pale yellow to a red-brown. The solution was kept at -78 °C for 60 min and then allowed to warm to room temperature, at which time approximately 75% (15 mL) solvent was removed in vacuo. The solution was cooled to -78 °C, and then cold (<0 °C) diethyl ether (50 mL) was added to the solution, thus precipitating 22 and an unidentified impurity. The suspension was rapidly filtered and washed with cold (<0 °C) diethyl ether (2 \times 20 mL) and then placed under vacuum (0.250 mmHg, 25 °C) for several hours. After the solution was stirred, 0.141 g of yellow-brown solid was obtained. From ¹H NMR (60 MHz), it appeared that 20 and an impurity had been formed in 1:1 ratio. Analytical data for 20: ¹H NMR (60 MHz, CD₃NO₂) δ 5.70 (s, 5 H), 8.2–8.7 (m, 6 H), 9.70 (d, 2 H, ³J_{HH} = 10.0 Hz); ¹³C NMR (300 MHz, CD₃NO₂) δ 92.074 (Cp), 137.016, 137.612, 138.104, 143.693, 158.866 (vinyl and aromatic carbons), 244.715 (carbonyl carbon).

Preparation of Dicarbonyl(1,2-benzocycloheptatrien-4-yl)(η^5 -cyclopentadienyl)ruthenium (19). The bromoalkene 23 (0.640 g, 2.93 mmol) was dissolved in THF (5 mL) and cooled to -78 °C. Butyllithium (2.0 mL, 1.5 M, 3.0 mmol) was added dropwise slowly to the bromoalkene solution, which went from colorless to green over the course of butyllithium addition. After the mixture was stirred at -78 °C for 30 min, R_pBr (0.800 g, 2.648 mmol, 0.91 equiv) in THF (10 mL) was added to the rapidly stirred alkyllithium solution at -78 °C. The solution was allowed to stir at -78 °C for 30 min and then allowed to warm to room temperature over a 1-h period. Solvent was removed in vacuo, and the residue was dissolved in the minimum amount of ethyl acetate-pentane (10:90 v/v) solution and eluted at 2.0 in./min on a 1 in. \times 12 in. low-pressure column (silica gel, 230–400 mesh, prepared with ethyl acetate-pentane, 10:90 v/v). Collection of the yellow band and removal of solvent in vacuo gave 0.521 g (54%) of orange oil (24): IR (neat) ν_{CO} 2018 (s), 1973 cm⁻¹ (vs); ¹H NMR (60 MHz, CDCl₃) δ 2.90 (d, 2 H, ³J_{HH} = 7.0 Hz), 5.33 (s, 5 H), 5.40 (m, 1 H), 6.20 (d, 1 H, ³J_{HH} = 8.50 Hz), 7.2–7.5 (m, 5 H); ¹³C NMR (25 MHz, CDCl₃) δ 34.213 (CH₂), 88.842 (Cp), 118.276, 125.099, 126.171, 126.366, 126.512, 126.610, 137.185, 137.331, 140.547, 142.692 (vinyl and aromatic carbons), 200.733 (C=O); mass spectrum, *m/e* 364 (M⁺). Anal. Calcd for C₁₈H₁₄O₂Ru: C, 59.50; H, 3.88. Found: C, 59.75; H, 3.90.

Preparation of Dicarbonyl(η^1 -3,4-benzocycloheptatrienyldiene)(η^5 -cyclopentadienyl)ruthenium Hexafluorophosphate (19). The σ complex 24 (0.200 g, 0.552 mmol) was dissolved in methylene chloride (5 mL) and cooled to -78 °C. Triphenylcarbenium hexafluorophosphate (0.214 g, 0.552 mmol) was dissolved in methylene chloride (10 mL) and cooled to -78 °C and then added via cannula to the rapidly stirred solution of σ complex at -78 °C. The σ complex solution darkened from yellow to orange-brown in color during the addition of the trityl salt. The solution was allowed to stir at -78 °C for 60 min and then allowed to warm to room temperature over a 60-min period. Solvent (approximately 10 mL) was removed and the solution cooled to -78 °C. Cold (<0 °C) diethyl ether (50 mL) was added rapidly, thus precipitating carbene complex 19 and an unidentified impurity. The suspension was filtered and washed with cold (<0

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°C) diethyl ether (2 × 20 mL). The resulting solid was then placed under vacuum (0.250 mmHg, 25 °C) for several hours, giving 0.250 g of yellow-brown solid containing (19) and an identified impurity. Analytical data for 19: ^1H NMR (CD_2Cl_2 , 100 MHz) δ 5.849 (s, 5 H), 8.020–8.460 (m, 5 H), 9.120 (d, 1 H, $^3J_{\text{HH}} = 10.13$ Hz), 9.699 (d, 1 H, $^3J_{\text{HH}} = 9.60$ Hz), 10.171 (s, 1 H); ^{13}C NMR (25 MHz, CD_3NO_2) δ 91.162 (Cp), 134.193, 136.338, 137.215, 138.433, 138.677, 139.067, 145.012, 155.636, 173.959, 176.104 (vinyl and ring carbons), 186.630 (carbene carbon), 200.227 (C \equiv O).

Preparation of Carbonylchloro(η^5 -cyclopentadienyl)-(tributylphosphine)ruthenium (27). Dodecacarbonyltriruthenium (1.00 g, 1.56 mmol) and freshly prepared cyclopentadiene (4.0 mL, 49 mmol) in 150 mL of heptane were refluxed for 3.0 h, during which time the initially orange solution became burgundy, then orange, and finally pale yellow. The yellow solution was cooled to 80 °C, and tri-*n*-butylphosphine (0.947 g, 4.68 mmol) was added. Gas evolution was immediate; however, the solution was allowed to stir for 20 min at 80 °C, by which time gas evolution had ceased. Solvent was removed in vacuo leaving an orange-brown oil which was dissolved in 125 mL of CHCl_3 and stirred overnight at room temperature. Silica gel (5.0 g, 60–200 mesh) was added to the solution, and solvent was removed in vacuo. The resulting yellow solid was placed on a 1 in. × 12 in. silica gel column (230–400 mesh) and eluted initially with 100 mL of pentane to remove residual tri-*n*-butylphosphine. Elution with ethyl acetate–pentane (1:9 v/v) resulted in collection of an orange band. Solvent was removed in vacuo, and the yellow crystalline product was dissolved in 10 mL of CH_2Cl_2 , to which were added 40 mL of hexane. Upon removal of approximately two-thirds of the solvent in vacuo and brief cooling to –78 °C, yellow crystals separated out. The crystals were filtered, washed with pentane (3 × 10 mL), and briefly dried under vacuum (0.200 torr, 25 °C) resulting in 1.26 g (62%) of 27: mp 99–100 °C; IR (hexane) ν_{CO} 1900 cm^{-1} (vs); ^1H NMR (60 MHz, CDCl_3) δ 1.0–2.3 (m, 27 H), 5.3 (s, 5 H); ^{13}C NMR (25 MHz, CDCl_3) δ 13.62 (C₄), 24.09 (C₂, $^2J_{\text{PC}} = 13.41$ Hz), 25.67 (C₃, $^3J_{\text{PC}} = 1.04$ Hz), 27.65 (C₁, $^1J_{\text{PC}} = 28.67$ Hz), 88.85 (Cp), 203.70 (C \equiv O, $^2J_{\text{PC}} = 20.65$ Hz); mass spectrum, m/e 432 (M^+), 404 ($\text{M}^+ - \text{CO}$), 366 ($\text{M}^+ - \text{C}_5\text{H}_6$). Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{OCIPRu}$: C, 50.05; H, 7.47. Found: C, 50.21; H, 7.48.

Preparation of Carbonyl(1,3,5-cycloheptatrien-1-yl)(η^5 -cyclopentadienyl)(tri-*n*-butylphosphine)ruthenium (28). A mixture of 1-, 2-, and 3-bromocycloheptatrienes (0.55 g, 3.24 mmol) was dissolved in 5.0 mL of THF and cooled to –78 °C with stirring. Butyllithium (2.2 mL, 1.5 M solution, 3.30 mmol) was added dropwise slowly, resulting in formation of the green-black color of the cycloheptatrienyllithiums. The solution was allowed to stir at –78 °C for 30 min. Compound 27 (0.70 g, 1.62 mmol, 0.50 equiv) was dissolved in THF (15.0 mL), cooled to –78 °C, and then added slowly to the cold (–78 °C) cycloheptatrienyllithium solution. Stirring was continued for 1 h at –78 °C, and then the solution was allowed to warm to room temperature over a 2-h period. Silica gel (4.0 g, 60–200 mesh) was added to the solution and solvent removed in vacuo. The resulting red-brown solid was placed on a 1 in. × 12 in. low-pressure, silica gel column (230–400 mesh) and upon elution with ethyl acetate–pentane (3% v/v),

a yellow band was collected. Upon removal of solvent in vacuo, an orange oil was obtained. The oil was rechromatographed as above; however, neutral grade II alumina was substituted for both meshes of silica gel. Solvent was removed in vacuo from the yellow band collected with ethyl acetate–pentane (3% v/v) which resulted in 0.200 g (25%) of orange oil 28: IR (neat) ν_{CO} 1900 cm^{-1} (vs); ^1H NMR (CDCl_3) δ 0.70–2.0 (m, 27 H), 2.4 (d, 2 H, $^3J_{\text{HH}} = 7.0$ Hz), 5.0 (s, 5 H), 5.2 (d, 1 H, $^3J_{\text{HH}} = 6.5$ Hz), 5.9–6.3 (m, 4 H); ^{13}C NMR (CDCl_3) δ 13.6 (butyl C₄), 24.1 (butyl C₂, d, $^2J_{\text{PC}} = 12.8$ Hz), 25.7 (butyl C₃, d, $^3J_{\text{PC}} = 2.1$ Hz), 28.8 (butyl C₁, d, $^1J_{\text{PC}} = 28.7$ Hz), 50.2 (C₇), 86.5 (Cp, d, $^3J_{\text{PC}} = 1.22$ Hz), 116.1, 122.8, 125.3, 132.1, 135.6 (C₂₋₆), 155.8 (C₁, d, $^2J_{\text{PC}} = 10.0$ Hz), 201.0 (C \equiv O, d, $^2J_{\text{PC}} = 20.0$ Hz); high-resolution mass spectrum, m/e calcd 488.1782, found 488.1798. Anal. Calcd for $\text{C}_{24}\text{H}_{38}\text{OPRu}$: C, 61.68; H, 8.07. Found: C, 61.73; H, 8.09.

Preparation of Carbonyl(η^5 -cycloheptatrienylidene)(η^5 -cyclopentadienyl)(tri-*n*-butylphosphine)ruthenium Hexafluorophosphate (29). The σ complex 28 (0.100 g, 0.205 mmol) was dissolved in 5.0 mL of CH_2Cl_2 and immediately cooled to –78 °C with stirring. Triphenylcarbenium hexafluorophosphate (0.080 g, 0.205 mmol) in 5.0 mL of CH_2Cl_2 at –78 °C was then added dropwise to the cold solution of σ complex 28 which resulted in color change of yellow to red. Stirring was continued at –78 °C for 8.0 h, followed by 1 h at room temperature. Solvent was then removed in vacuo until 2–3 mL of solvent remained. Subsequently, the solution was cooled to –78 °C and 45 mL of diethyl ether was added which resulted in formation of a red precipitate. The suspension was immediately filtered via coarse glass frit and washed with cold diethyl ether (0 °C, 2 × 15 mL). Drying of the red solid (0.200 torr, 25 °C) resulted in 0.080 g (64%) of carbene complex 30: mp 110–111 °C dec; IR (CDCl_3) ν_{CO} 2020, 1980 cm^{-1} ; ^1H NMR (60 MHz, CD_3NO_2) δ 0.3–1.9 (m, 27 H), 5.2 (s, 5 H), 6.9–7.3 (m, 2 H), 7.5–7.9 (m, 2 H), 9.1 (d, 2 H, $^3J_{\text{HH}} = 11.0$ Hz); ^{13}C NMR (25 MHz, CD_3NO_2) δ 14.0 (butyl C₄), 25.0 (butyl C₂, d, $^2J_{\text{PC}} = 13.4$ Hz), 26.8 (butyl C₃), 29.6 (butyl C₁, d, $^1J_{\text{PC}} = 29.3$ Hz), 91.4 (Cp), 135.2 (C_{3,6}), 145.5 (C_{4,5}), 168.1 (C_{2,7}), 179.0 (C \equiv O), 256.2 (C₁). Anal. Calcd for $\text{C}_{24}\text{H}_{38}\text{OF}_6\text{P}_2\text{Ru}$: C, 47.54; H, 6.06. Found: C, 47.73; H, 5.81.

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Registry No. 9, 103533-75-1; 10, 14878-26-3; 11, 103533-74-0; 12, 103533-76-2; 13, 103533-77-3; 15, 103533-79-5; 19, 103533-85-3; 20, 103533-82-0; 21, 66031-67-2; 22, 103533-80-8; 23, 97719-86-3; 24, 103533-83-1; 27, 32613-26-6; 28, 103533-86-4; 29, 103533-88-6; RpBr, 32613-75-5; Ru3(CO)12, 15243-33-1; sodium dicarbonyl-(δ^5 -cyclopentadienyl)ruthenate, 42802-20-0; 1-bromocycloheptatriene, 32743-67-2; 2-bromocycloheptatriene, 3046-02-4; 3-bromocycloheptatriene, 3046-03-5; cyclopentadiene, 542-92-7.