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Carbene Migratory Insertions: Preparation of the First Second-Row Late-Transition-Metal Alkyl-Substituted Carbene Complex and Comparison of Its Migratory Insertion with That of Its Iron Analogue

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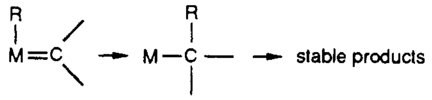
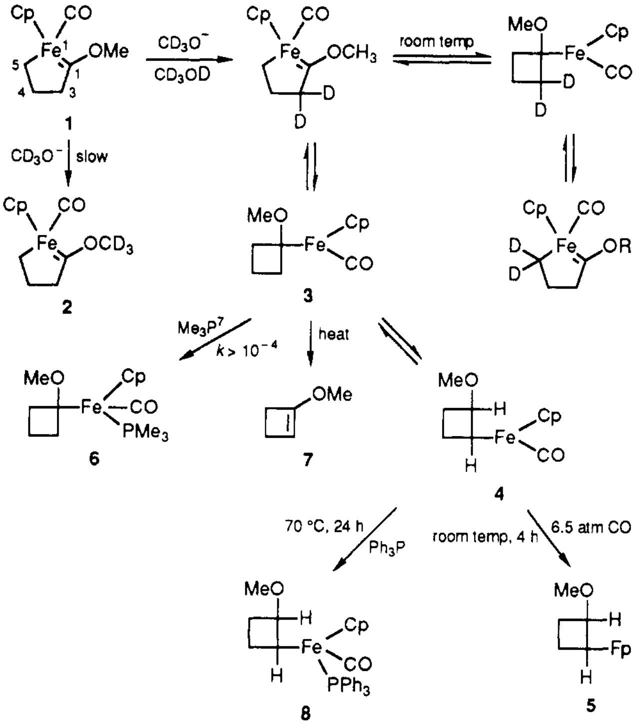
Summary: **The first stable second-row late-transition-metal carbene complex substituted on the metal with an alkyl group (20, M = Ru) has been prepared. Comparison with its iron analogue shows carbene migratory insertion in the iron compound to be at least 10^7 times faster than in the ruthenium complex. This dramatic difference is ascribed to the stronger carbon–metal double bond in the ruthenium complex.**

First- or second-row group 7 or 8 transition metals substituted with both alkyl (or aryl) and carbene ligands are exceedingly rare; to our knowledge, prior to our work[1] only two examples of iron complexes had been recorded.[2,3] In most cases, this void is presumably due to the exothermicity[5] of the so-called carbene migratory insertion[6] reaction (perhaps more appropriately designated simply as a 1,2-rearrangement) which gives an electron-deficient intermediate that rapidly goes on to stable products:

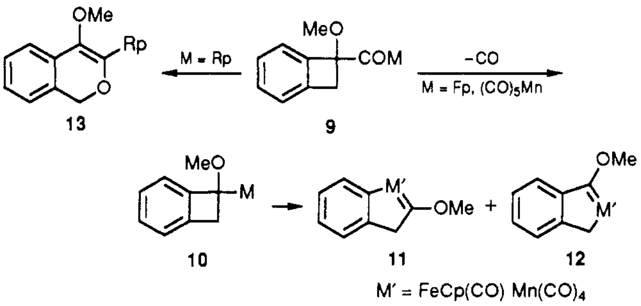


In recent years we have found that the simple expedient of stabilizing the carbene with an electron-donating substituent and introducing strain into the rearranged product can retard the migratory insertion enough to permit isolation and characterization of both iron and selected manganese alkyl- and aryl-substituted carbene complexes.[1] Furthermore, in some cases strong evidence for facile migratory insertion at room temperature has been demonstrated.[1b,d-f] The most thoroughly examined example is summarized in Scheme I.

Scheme I



Scheme II[a]



[a] Legend: Fp = dicarbonyl(η^5-cyclopentadienyl)iron; Rp = dicarbonyl(η^5-cyclopentadienyl)ruthenium.

A comparison of carbene migratory insertions in ruthenium and iron complexes would be of interest because both are catalytically active in the Fischer–Tropsch reaction, a reaction in which this rearrangement may play a key role.[8] We therefore undertook to prepare the ruthenium analogue of the iron complex 1 with the ultimate goal of comparing migratory insertions.

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(1) (a) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4*, 944. (b) Stenstrom, Y.; Jones, W. M. *Organometallics* **1986**, *5*, 178. (c) Stenstrom, Y.; Klauck, G.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Organometallics* **1986**, *5*, 2155. (d) Stenstrom, Y.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Organometallics* **1987**, 2079. (e) Conti, N. J.; Jones, W. M. *Organometallics* **1988**, *7*, 1666. (f) Conti, N. J.; Crowther, D. J.; Tivakornpannarai, S.; Jones, W. M. *Organometallics* **1990**, *9*, 175. (g) Crowther, D. J.; Tivakornpannarai, S.; Jones, W. M. *Organometallics* **1990**, *9*, 739. (h) Tivakornpannarai, S.; Jones, W. M. *Organometallics* **1991**, *10*, 1827.

(2) Rosenblum, M.; Price, T.; Priester, W.; Klemarczy, P. *J. Organomet. Chem.* **1977**, *139*, C27.

(3) Recently a few stable third-row late-transition-metal complexes have been reported.[4] In its simplest terms, this is probably because the stronger carbon–metal double bond compensates for the strength of the carbon–carbon bond formed as a result of the insertion.

(4) (a) Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811. (b) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 7578. (c) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2060. (d) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 4129. (e) Bleeke, J. R.; Xie, Y. F.; Peng, W. J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118. (f) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 464. (g) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6232. (h) O'Connor, J. M.; Pu, L.; Woolard, S.; Chadha, R. K. *J. Am. Chem. Soc.* **1990**, *112*, 6731. (i) Bleeke, J. R.; Peng, W. J.; Xie, Y. F.; Chiang, M. Y. *Organometallics* **1990**, *9*, 113. (j) Bleeke, J. R.; Xie, Y. F.; Bass, L.; Chiang, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 4703.

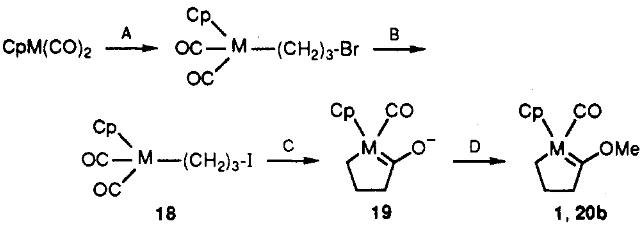
(5) First suggested by: Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121.

(6) In recent years, carbene migratory insertions have become ubiquitous as postulated mechanistic steps in multistep organometallic reactions. For leading references, see ref 1 and 4f.

(7) Patton, J. T. Unpublished results, University of Florida.

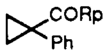
(8) For an excellent discussion of the Fischer–Tropsch reaction, including a theoretical study that addresses the question of the feasibility of carbene migratory insertions at a single ruthenium atom, see: Carter, E. A.; Goddard, W. A., III. *Organometallics* **1988**, *7*, 675.

Scheme III. Synthesis of Compounds 1 and 20b[a]



[a] Reagents and conditions: (A) for Fe, 1.3 equiv of KFp added to 1.0 equiv of 1,3-dibromopropane in THF at 0 °C (74%) and for Ru, NaRp from 1 equiv of Rp_2 added to 1.0 equiv of 1,3-dibromopropane in THF at −78 °C to room temperature overnight (95%); (B) for Fe, 1.0 equiv of bromide with 3.5 equiv of NaI in acetone at 45 °C (98%), and for Ru, 1.0 equiv of bromide and 3.0 equiv of NaI in acetone at room temperature overnight (68%); (C) for Fe, 1.0 equiv of iodide and 2.5 equiv of *t*-BuLi in ether at −78 to −30 °C, and for Ru, 1.0 equiv of iodide and 2.5 equiv of *t*-BuLi at −100 to −15 °C; (D) for Fe and Ru, Me_3OBF_4 added to pH 5, quench with degassed water (Fe, 55%; Ru, 49%).

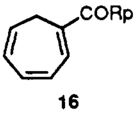
In our work, to date, all iron and manganese alkyl- and aryl-substituted carbene complexes have been prepared by α-elimination from 16-electron σ complexes, in most cases originating from acyl complexes.[1] This has been particularly useful for the preparation of benzannelated complexes,[1c,g] as illustrated in Scheme II. As a test case, we therefore initially attempted to prepare the ruthenium carbene complexes **11** and **12** (M′ = RuCp(CO)) from the benzocyclobutenyl acyl complex **9** (M = Rp (Rp = $RuCp(CO)^2$). However, to our surprise, although the acyl complex could be readily prepared, all attempts to effect decarbonylation failed. For instance, photolysis of **9** (M = Rp) for 20 h using a Pyrex filter showed no reaction, while higher frequency light led to a multitude of products, none of which appeared to be either of the desired carbene complexes. Similarly, thermolysis of **9** (M = Rp) below 80 °C showed no reaction, while more extreme conditions (85 °C for 4 days) led to ring expansion to **13**.[9] Apparently, this reluctance for ruthenium acyl complexes to undergo decarbonylation is rather general; on searching the literature, we have found no examples of either heat- or light-induced decarbonylation of Rp–acyl complexes[10] and, in our hands, at least three other acyl complexes (**14**–**16**[12]) have been found to be completely inert to either photolysis or thermolysis.[12,13] An alternate and more direct route to late-transition-metal cycloalkenes was therefore developed. This is illustrated in Scheme III for the preparation of **1** and **20b** (49% and 53% yields for the ring-closure/alkylation steps, respectively); ethylation of **19** (M = RuCp(CO)) increased the yield to 67%, and although the method works well for each metal, success is very sensitive to reaction conditions, particularly the alkylation step.[15,16]



14

$PhCH_2CORp$

15



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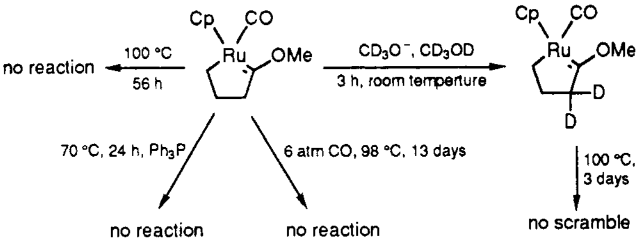
Scheme IV



The ruthenium metallacycle **20b** is a stable yellow oil at room temperature and, to our knowledge, is the first recorded stable second-row late-transition-metal complex substituted with both a carbene and an alkyl group. Of most interest to us was a comparison of carbene migratory insertions of **1** with those of **20b**. Significant chemistry of **1** is summarized in Scheme I.[1] Comparable chemistry for **20b** is summarized in Scheme IV. From a comparison of these schemes, two major differences emerge. First, exchange of CD_3O for CH_3O is significantly faster in the ruthenium complex than in its iron counterpart (3 h vs several days at room temperature for essentially complete exchange). This is counter to expectation based on metal electronegativities (or anion stability at the metal center)[17] and presumably is simply a reflection of less steric hindrance to attack by CD_3O^- at the carbene carbon due to the expected longer carbon–metal bond. The second and more significant conclusion is that carbene migratory insertion in the five-membered ruthenium carbene complex is much slower than in its iron analogue; indeed, there is no sign of rearrangement whatsoever when the deuterated Ru complex is heated at 100 °C for 3 days nor is any trapped product detected when the undeuterated complex is heated in the presence of 6 atm of CO at 98 °C for 13 days. Since 5% should be easily detected, a minimum half-life of about 10^6 s at 100 °C for the rearrangement is reasonable. This corresponds to a $\Delta G^\ddagger$ value of about 33 kcal/mol, which can be compared with a maximum $\Delta G^\ddagger$ value of 23 kcal/mol for the corresponding iron complex.[18] Thus, the barrier to insertion for the ruthenium complex **20b** is at least 10 kcal/mol higher than for the iron analogue or, to put it another way, if the entropies of activation

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[9] Spectral properties of **13**: ^{1}H NMR (C_6D_6, δ, ppm) 3.58 (3 H, s, OMe), 4.70 (5 H, s, Cp), 4.79 (2 H, s, CH_2), 6.80–7.30 (4 H, m, aryl); ^{13}C NMR (C_6D_6, 75 MHz, δ, ppm) 60.17 (CH_2), 69.15 (OMe), 88.25 (Cp), 116.44 (vinyl), 123.57, 124.65, 127.77, 128.47, 147.99, 158.46 (aryl), 199.65 (CO).

[10] Wrighton[11] has shown that Rp–alkyl complexes undergo photoinduced decarbonylation.

[11] Wrighton, M. S.; Kazlauskas, R. J. *Organometallics* **1982**, *1*, 602.

[12] Lisko, J. R.; Jones, W. M. *Organometallics* **1986**, *5*, 1890.

[13] Chemically induced decarbonylation with reagents such as amine oxides led to intractable mixtures with no evidence of the desired product. This was not surprising, due to the known instability of metal carbene complexes to such oxidizing agents.[14]

[14] Cf.: Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.

[15] Details for our best preparations to date for each is provided in the supplementary material. Properties of 1[1b] and the alkyl bromide precursor to **18a**[15] have been previously reported. Properties of other new compounds are as follows. **18a**: yellow oil; ^{1}H NMR (C_6D_6) δ 3.9 (s, 5 H), 2.85 (triplet, 2 H), 1.8 (pentet, 2 H), 1.1 (triplet, 2 H); IR (hexane, cm^{-1}) 2013.1, 1960.7. **18b**: yellow crystals; mp 38.0–39.0 °C; IR (hexane, cm^{-1}) 2023, 1965; ^{1}H NMR (C_6D_6, 300 MHz, δ, ppm) 1.36–1.42 (2 H, CH_2, t), 1.86–1.98 (2 H, CH_2, m), 2.81–2.88 (2 H, CH_2, t), 4.40 (5 H, s, Cp); ^{13}C NMR (C_6D_6, 75 MHz, δ, ppm) −4.24 (CH_2), 10.00 (CH_2), 43.93 (CH_2), 88.38 (Cp), 202.47 (CO). Anal. Calcd for $C_{10}H_{11}IO_2Ru$: C, 30.70; H, 2.84. Found: C, 30.73; H, 2.80. **20b**: yellow oil; IR (hexane, cm^{-1}) 1951; ^{1}H NMR (C_6D_6, 300 MHz, δ, ppm) 1.68–2.04 (2 H, m, CH_2), 2.10–2.20 (1 H, m, CH), 2.36–2.47 (1 H, m, CH), 2.51–2.68 (1 H, m, CH), 2.79–2.88 (1 H, m, CH), 3.74 (3 H, s, OMe), 4.73 (5 H, s, Cp); ^{13}C NMR (C_6D_6, 74 MHz, δ, ppm) 7.65 (CH_2), 31.39 (CH_2), 60.13 (CH_2), 66.53 (OMe), 86.89 (Cp), 207.92 (CO), 325.02 (C=Ru). Anal. Calcd for $C_{11}H_{14}O_2Ru$: C, 47.30; H, 5.02. Found: C, 47.40; H, 5.10.

[16] This method may have the potential to be rather general, although, to date, it failed for **20** (M = W(CO)), where attempted ring closure gave only cyclopropane and Wp^-.

[17] Cf.: (a) King, R. B.; Pohl, R. L.; Dessy, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 5121. (b) Darensbourg, M. Y.; Kao, S. C.; Spillett, C. T.; Ash, C.; Lusk, R.; Park, K. *Organometallics* **1985**, *4*, 83. (c) Norton, J. R.; Warner, K. E.; Martin, B. D. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

[18] Attempts to obtain accurate kinetic data for contraction of **1** (using four different kinetic techniques) have not yet provided reliable enough rate constants for accurate determination of activation parameters. However, a minimum rate constant of 10^{-4} s^{-1} at 20 °C is secure.[19]

[19] Patton, J. Unpublished results, University of Florida.

for contraction of the iron and ruthenium complexes are the same, at room temperature the iron complex **20b** undergoes migratory insertion at least 10^7 times faster than its ruthenium analogue.

The net result of a carbene migratory insertion is formation of a carbon–carbon single bond at the expense of a carbon–metal double bond. Inasmuch as rearrangement of **1** and **20b** is endothermic, their transition states should resemble the 16-electron intermediate products and differences in their respective energies should therefore be reflected in differences in the strengths of their carbon–metal double bonds.[20] The generally accepted presumption that second-row transition-metal carbon–metal bonds are stronger than those of first-row metals[21] therefore provides an attractive explanation for this difference in rates.

Acknowledgment. This work was supported by the National Science Foundation, to whom we are most grateful.

Supplementary Material Available: Text giving experimental procedures for the preparation of **20a** and **20b** by the ring-closure method (5 pages). Ordering information is given on any current masthead page.

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(20) Carter, E. A.; Goddard, W. A., III. *Organometallics* **1988**, *7*, 675.

(21) Cf.: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 100.

A New Strategy for the Synthesis of Homologously Pure Linear Polystannane Oligomers†

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Summary: The reagent **6** is utilized for the stepwise synthesis of linear polystannane oligomers in which hydrostannolysis is employed as the Sn–Sn bond-forming reaction, and DIBAL-H is used to regenerate a new Sn–H functionality for extended chain growth through repetition of the two-step reaction sequence. The electronic spectra of these oligomers are influenced by chain length and the specific placement of substituents, as demonstrated by the homologous series **7**, **9**, and **13–15** and the phenylated di- and tristannanes **18–20**.

New types of protecting groups should greatly aid molecular engineering approaches to inorganic or organometallic materials that require the construction of complex structures via rational routes.[1] Herein, we describe application of the β-alkoxy substituent as a protecting group for the programmable stepwise synthesis of linear polystannane oligomers $R–(R_2Sn)_n–R$ (**1**), a class of compounds that exhibit interesting optical properties[2] and which, to date, have not been routinely available for study.[3]

Our approach to polystannane oligomers is based on the tin–tin bond-forming hydrostannolysis reaction,[4] which has been successfully used for the high-yielding syntheses of linear tri- and tetrastannanes according to reaction 1.[5]

$$\mathrm{H\text{-}(R_2Sn)_n\text{-}H} \quad + \quad 2\ \mathrm{R_3SnNMe_2} \xrightarrow[n\,=\,1\text{ or }2]{} \mathrm{R_3Sn\text{-}(R_2Sn)_n\text{-}SnR_3} \quad + \quad 2\ \mathrm{HNMe_2} \qquad (1)$$

However, in order to apply this synthetic methodology to the construction of higher order homologues, a protecting group is required that can be removed, after hydrostannolysis, to reveal a new functionality that can then serve as the site for extended chain growth of the polystannane backbone. As Schemes I and II show, this requirement is met by the β-alkoxy substituent.

An equimolar mixture of the diorganotin dihydride **2** and the diorganotin dichloride **3** generates, in situ, the diorganotin hydridochloride species **4**, and this species is more reactive toward hydrostannation than **2** (Scheme I).[6] Thus, addition of a radical initiator and ethyl vinyl ether to a solution of **4** in hexane regiospecifically produces compound **5**,[7] which is subsequently converted, without

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† Contribution No. 8431.

(1) Gomez, F. A.; Johnson, S. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1991**, *113*, 5915.

(2) (a) Drenth, W.; Janssen, M. J.; Van Der Kerk, G. J. M.; Vliegenthart, J. A. *J. Organomet. Chem.* **1964**, *2*, 265. (b) Drenth, W.; Noltes, J. G.; Bulten, E. J.; Creemers, H. M. J. C. *J. Organomet. Chem.* **1969**, *17*, 173. (c) Adams, S.; Dräger, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1255.

(3) (a) Neumann, W. P.; Konig, K. *Justus Liebigs Ann. Chem.* **1964**, *677*, 1. (b) Creemers, H. M. J. C.; Noltes, J. G. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 382. (c) Jousseaume, B.; Chanson, E.; Bevilacqua, M.; Saux, A.; Pereyre, M.; Barbe, B.; Petraud, M. *J. Organomet. Chem.* **1985**, *294*, C41. (d) Reference 2c.

(4) (a) Neumann, W. P. *The Organic Chemistry of Tin*; Wiley: New York, 1970. (b) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, U.K., 1980.

(5) Sommer, R.; Schneider, B.; Neumann, W. P. *Justus Liebigs Ann. Chem.* **1966**, *692*, 12.

(6) Neumann, W. P.; Pedain, J. *Tetrahedron Lett.* **1964**, *36*, 2461.

(7) To a solution of 10.34 g (34 mmol) of dichlorodibutylstannane in 80 mL of hexane was first added 8.00 g (34 mmol) of dibutylstannane, followed by 20 mL (210 mmol) of ethyl vinyl ether and 100 mg (0.61 mmol) of azobis(isobutyronitrile). The mixture was then placed into a 150-mL heavy-walled glass Schlenk tube, which was sealed and heated at 45 °C for 18 h. After it was cooled, the reaction vessel was opened in a glovebox, the solvents were removed in vacuo, and the residue was filtered through a $^1/_4$-in. pad of Celite in a glass pipet equipped with a plug of Kimwipe to provide 22.16 g (65 mmol; 96% yield) of the desired product as a clear colorless oil. The purity of this material, as determined by ^{1}H NMR spectroscopy, is adequate for the preparation of **6a**. Note: attempts to further purify **5a** by distillation under reduced pressure result in substantial decomposition. ^{1}H NMR (500 MHz, benzene-d_6): δ 0.83 (t, 3 H, J = 6.9 Hz), 0.89 (t, 6 H, J = 7.0 Hz), 1.23 (m, 4 H), 1.35 (sext, 4 H, J = 7.7 Hz), 1.65 (t, 2 H, J = 7.6 Hz), 1.69 (m, 4 H), 2.97 (q, 2 H, J = 7.0 Hz), 3.28 (t, 2 H, J = 7.5 Hz [$^3J(^{119}\mathrm{Sn}–^1\mathrm{H})$ = 68.5 Hz]).

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