erably, with **7a** containing only terminal carbonyls and **7b** containing both terminal and bridging carbonyl stretching vibrations. The $^{31}P\{^1H\}$ NMR spectra show singlets at δ 30.4 for **7a** and at δ 42.9 for **7b**, in the regions typical for bridging DPPM[27] and chelated DPPE,[28] respectively. Compounds **7a** and **7b** have been elucidated by X-ray structural determinations.[29,30]

For $[Ru_2(CO)_4(\mu\text{-}O_2CCH_3)(DPPM)_2][PF_6]\cdot 2(CH_3)_2CO$, an ORTEP diagram of the cation is shown in Figure 1. Both metals have almost undistorted octahedral geometries and are bridged by the two DPPM groups in a mutually trans arrangement and by the acetate group. The Ru–Ru separation of 2.841 (1) Å is consistent with a single bond, as expected for a Ru(I)/Ru(I) dimer, and this relatively short separation results in a slight twist of the substituents on each metal from an exactly eclipsed conformation, yielding torsion angles about the Ru–Ru bond of between 17.3 (2)° and 20.6 (4)°. There is a pronounced difference in the Ru–C distances for the axial (1.914 (6) Å) and equatorial (1.825 (8) Å) carbonyl ligands, possibly reflecting either the π-donor ability of the acetate group opposite the equatorial CO's or the large trans influence of the metal–metal bond.[31] Structurally this species resembles $[Ru_2(\mu\text{-}OB(F)OH)(CO)_4(i\text{-}PrO)_2PN(Et)P(O\text{-}i\text{-}Pr)_2)_2][BF_4]$[9a] which has a comparable Ru–Ru distance of 2.814 (1) Å.

An ORTEP representation of the complex cation of $[Ru_2(CO)_2(\mu\text{-}CO)_2(\mu\text{-}O_2CMe)(DPPE)_2][PF_6]$ (**7b**) is shown in Figure 2. The Ru–Ru separation in this dimer (2.751 (1) Å) is somewhat shorter than in **7a** but is still consistent with a normal single bond. If we ignore this bond, the complex can be described as a bioctahedron sharing an edge at the bridging carbonyl groups. Angles about the Ru atoms range from 82.9 (2)° to 96.7 (4)°, indicating only slight distortions from idealized octahedral geometries. The small bite of the bridging acetate group causes a slight tilt, by 21.5 (2)°, of the two Ru equatorial planes and puckering about the axis containing the bridging carbonyl ligands. All other parameters within the complex are as expected.

Formation of a diphosphine-bridged species with DPPM but a chelating-diphosphine species with DPPE is not unexpected on the basis of the normal tendencies of these groups; however, it does result in two interesting variations in these unusual types of diphosphine-containing diruthenium(I) complexes. The convenient routes to these complexes, reported herein, significantly extend the known types of diruthenium(I) complexes, which until now have been rather scarce. It is anticipated that with these diphosphine- and dithioether-bridged species the chemistry associated with adjacent Ru(I) centers can be probed.

Acknowledgment. This work at the University of Alberta was supported by the Natural Sciences and Engineering Research Council (Canada) and the University of Alberta. We thank Dr. P. H. van Rooyen and coworkers in the Structural Chemistry Division of the CSIR, Pretoria, South Africa, for X-ray data collection, on compounds **7a** and **7b**, providing computing programs, and useful discussions.

Registry No. **1a**, 24846-20-6; **1b**, 96317-57-6; **2a**, 108294-67-3; **2b**, 114550-94-6; **3a**, 114550-93-5; **3b**, 114550-95-7; **4a**, 114550-96-8; **4b**, 114550-98-0; **5a**, 114550-97-9; **5b**, 114550-99-1; **6**, 114551-05-2; **7a**$\cdot 2(CH_3)_2CO$, 114551-02-9; **7b**, 114551-04-1; $[Ru_2(CO)_4(\mu\text{-}I)_2(\mu\text{-}DPPM)]$, 103538-15-4; $[Ru_2(CO)_4(O_2CCH_3)_2]_n$, 89689-03-2; Ru, 7440-18-8.

Supplementary Material Available: Tables of fractional coordinates, anisotropic thermal parameters, and listings of bond lengths and angles for compounds **7a** and **7b** (18 pages); listings of structure factor amplitudes for **7a** and **7b** (57 pages). Ordering information is given on any current masthead page.

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(25) Anal. Calcd for $[Ru_2(CO)_4(\mu\text{-}O_2CMe)(\mu\text{-}DPPM)_2][PF_6]\cdot 2(CH_3)_2CO$: C, 53.07; H, 4.24. Found: C, 52.33; H, 4.29. mp: 128 °C. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2023 s, 2006 s, 1963 m, 1934 w; $\nu((Me)_2CO)$ 1713 m; $\nu(CO_2)$ 1541 s; $\nu(PF_6)$ 847 m. $^{31}P\{^1H\}$ NMR (121 MHz, acetone-d_6, 30 °C): δ 30.36 (s). ^1H NMR (500 MHz, acetone-d_6 30 °C): δ 0.76 (s, *Me*), 2.08 (s, *Me*), 4.43 (dt, CH_2, J(HH) = 15.2, J(PCH) = 5.5 Hz), 4.93 (dt, CH_2, J(HH) = 15.2, J(PCH) = 4.2 Hz), 7.41 (m, *Ph*), 7.47 (m, *Ph*), 7.56 (m, *Ph*), 7.64 (m, *Ph*).

(26) Anal. Calcd for $[Ru_2(CO)_2(\mu\text{-}CO)_2(\mu\text{-}O_2CMe)(DPPE_2)][PF_6]$: C, 52.98; H, 3.19. Found: C, 52.95; H, 3.88. mp: 225 °C. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2004 s, 1944 sh, 1750 m; $\nu(CO_2)$ 1549; $\nu(PF_6)$ 847 s. $^{31}P\{^1H\}$ NMR (202 MHz, acetone-d_6, 30 °C): δ 42.85 s. ^1H NMR (500 MHz, acetone-d_6, 30 °C): δ 0.90 (s, *Me*), 3.00 (br s, C_2H_4), 3.14 (br s, C_2H_4), 7.33 (m, *Ph*), 7.50 (m, *Ph*), 7.57 (m, *Ph*), 7.82 (m, *Ph*).

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(28) Pomeroy, R. K.; Wijesekera, K. S. *Can. J. Chem.* **1980**, *58*, 206.

(29) Crystal data for $[Ru_2(CO)_4(\mu\text{-}O_2CCH_3)(\mu\text{-}DPPM)_2][PF_6]\cdot 2(CH_3)_2CO$: $C_{62}H_{59}F_6O_8P_5Ru_2$; M_r 1403.14; monoclinic, space group $C2$; a = 19.354 (3) Å, b = 15.126 (2) Å, c = 10.780 (2) Å; β = 91.68 (1)°; V = 3154.5 Å^3; Z = 2; D_{calcd} = 1.48 g cm^{-3}; λ(Mo Kα) = 0.710 73 Å; μ = 0.594 mm^{-1}; $F(000)$ = 1423.98. A yellow crystal with dimensions 0.37 × 0.33 × 0.20 mm was used. Cell parameters and intensity data were measured on an Enraf-Nonius CAD4F diffractometer with graphite-monochromated Mo Kα radiation in the range $3 < \theta < 30°$. Data were corrected for Lorentz and polarization effects and for absorption (North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351). The structure was solved by Patterson and difference electron density synthesis methods using the ShelX program (Sheldrick, G. M. *Computing in Crystallography*; Delft University: Delft, 1978) and was refined to a current R_w of 0.041 for 350 parameters and 4338 reflections with $F_o \le 5\sigma(F_o)$ and a weighting scheme of $w = 1.7506/\sigma^2(F_o)$. The molecule resides on a crystallographic twofold rotation axis with acetate carbon atoms and the counterion phosphorous atom on special positions. Phenyl hydrogens were idealized and not refined, and acetate hydrogens were omitted since these could not be accommodated by the twofold symmetry. The y coordinate of ruthenium was fixed to define the origin. Non-hydrogen atoms, except for fluorine atoms and solvate carbon and oxygen atoms, were refined anisotropically; others were refined isotropically.

(30) Crystal data for $[Ru_2(CO)_2(\mu\text{-}CO)_2(\mu\text{-}O_2CCH_3)(DPPE)_2][PF_6]$: $C_{58}H_{51}F_6O_6P_5Ru_2$; M_r 1315.0; monoclinic, space group $P2_1/c$; a = 16.141 (5) Å, b = 13.904 (5) Å, c = 25.189 (4) Å; β = 94.11 (3)°; V = 5638.36 Å^3; Z = 4; D_{calcd} = 1.55 g cm^{-3}; λ(Mo Kα) = 0.710 73 Å; μ = 0.659 mm^{-1}; $F(000)$ = 2655.96. A crystal with dimensions 0.40 × 0.15 × 0.08 mm was used. Data collection (to θ = 23°), data reduction, and structure solution were performed as described in ref 24. The structure was refined as a blocked matrix to a current R_w of 0.053 for 726 parameters and 5120 reflections with $F_o \le 2\sigma(F_o)$ and a weighting scheme of $w = 1.2565/\sigma^2(F_o)$. Hydrogen atoms were idealized and not refined. Non-hydrogen atoms were refined with anisotropic and hydrogen atoms were assigned isotropic thermal parameters.

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Generation of a 1-Ferracyclobutene from Thermal and Photolytic Induced Rearrangement of α-Ethoxycyclopropyl σ Complexes of Iron

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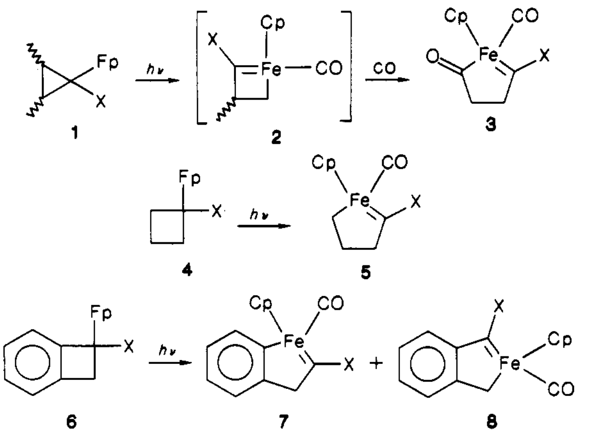
Summary: A 1-ferracyclobutene (**11**) has been isolated from photolysis of the (η^5-cyclopentadienyl)dicarbonyliron complex of 1-ethoxycyclopropane (**9a**). This same material is apparently also formed from thermolysis of the Ph_3P-substituted σ-complex **9b**. The chemistry of this highly unstable metallacycle includes migratory CO insertion to form the ferracyclopentenones **12a** and **12b** (in the presence of added CO and Ph_3P, respectively), ring contraction to the 16-electron intermediate **10**, and ring opening (tentative) to the terminally substituted π-allyl complex **14**. The 16-electron intermediate **10** also slowly ring opens to the centrally substituted π-allyl complex **13**.

In recent papers,[1] we have reported results of studies of the rearrangements of the cyclopropyl, the cyclobutyl, and the benzocyclobutenyl iron σ complexes **1**, **4**, and **6**, respectively. From our observations, we have concluded that carbon (sp^3 or sp^2 hybridized) can be induced to rearrange from a saturated carbon to an electron-deficient iron atom to give a metallcyclic carbene complex (an α-elimination) if three conditions are met: (1) the reaction is initiated by photolysis; (2) the resulting carbene moiety is stabilized by an electron donor (methoxy in **3**, **5**, **7**, and **8**; thiophenyl in **7** and **8**; (3) ring strain is relieved at some point in the overal reaction.



Fp = CpFe(CO)$_2$

From further work on the cyclopropyl system, we can now report: (1) evidence for the first thermally induced rearrangement of an alkyl group from a saturated carbon to iron;[2] (2) spectral evidence for the previously postulated ferracyclobutene intermediate **2**; (3) evidence for competitive and relatively slow irreversible ring opening of **10** and probably **11** to give the π-allyl complexes **13** and **14**, respectively; (4) evidence for the reversibility of both ring expansions in Scheme II.

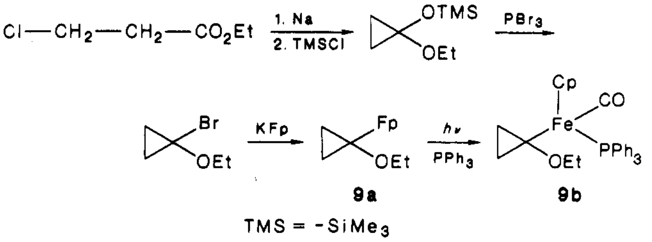
For this work the cyclopropyl σ-complex **9a** was synthesized as shown in Scheme I.[3] The phosphine-substituted complex **9b** was prepared by photolysis of **9a** in the presence of 1 equiv of PPh$_3$.

Photolysis of **9a** in benzene-d_6 for 4 h or thermolysis of **9b** (at 75 °C for 47 h) gave the carbene complexes **12a** and **12b**, respectively. The latter is the first example of a thermally induced α-elimination of an alkyl group for iron.[2,4]

When the photolysis of **9a** was monitored by ^{13}C NMR, it was noted that a new Cp resonance appeared rather early in the reaction, increased to a maximum intensity after about 2 h, and rather rapidly disappeared (only a relatively small amount remained after 4 h). Although too unstable for complete characterization, we believe that this intermediate is the ferracyclobutene **11**[5] for the following reasons. First, when the reaction was interrupted after 2 h, the ^{13}C NMR spectrum of the mixture showed, in addition to the rearranged acylcarbene complex **12a**, a new terminal carbonyl resonance (224 ppm) and a new, very low-field resonance at 335 ppm. The latter is characteristic of carbene complexes of this type.[1] Second, when the reaction was interruped after 30 min of photolysis, the reaction mixture showed only one low-field ^{13}C resonance at 335 ppm. However, when carbon monoxide was bubbled through the solution, this resonance rapidly disappeared and a new peak appeared at 342 ppm. The latter peak corresponds to **12a**. Third, when the reaction was interrupted after 30 min and triphenylphosphine was added, the resonance at 335 ppm disappeared and was replaced by a doublet at 342 ppm which corresponds to **12b**. Finally, despite its instability, a quantity of pure **11** (red solid) sufficient for a ^{1}H NMR spectrum was obtained by photolysis of a relatively large quantity of the σ complex followed by rapid low-temperature (−50 °C) flash chromatography over silica gel. The spectrum was completely consistent with structure **11**. This material was too unstable for further characterization.

Photolysis of a solution of **9a** in the presence of added CO gives the carbene complex **12a** more cleanly than in its absence. Suspecting that this might be due to photodecomposition of **12a** via **11**, photolysis of a reaction mixture (in the absence of added CO) was continued until the ^{13}C resonances of the "impurities" (which grew at the expense of **12a**) reached a maximum. Careful and repeated

Scheme I



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(1) (a) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4* 944–946. (b) Stenstrom, Y.; Jones, W. M. *Organometallics* **1986**, *5*, 178–180. (c) Stenstrom, Y.; Klauck, G.; Koziol, A. E.; Palenik, G. J.; Jones, W. M. *Organometallics* **1986**, *5*, 2155. (d) Strenstrom, Y.; Koziol, A. E.; Palenik, G. J.; Jones, W. M. *Organometallics* **1987**, *6*, 2079.

(2) Grubbs provided evidence for a thermally induced rearrangement of this type in a nickel compound. (Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7418–7420).

(3) The cyclopropane silyl ketal was prepared by the method of: Ruhlmann, K. *Synthesis* **1971**, 326. The cyclopropyl bromo ether was prepared by the method of: Goadwood, R. C. *Tetrahedron Lett.* **1984**, 5851.

(4) Compound **9a**: IR (CHCl$_3$) 1999, 1943 cm^{-1}; ^{1}H NMR (60 MHz, C_6D_6) 4.4 (s, 5 H, Cp), 3.4 (q, 2 H, OCH$_2$), 1.1 (t, 3 H, CH$_3$), 1.0–0.4 ppm (m, 4 H, CH$_2$); ^{13}C NMR (75 MHz, C_6D_6), 217.6 (MCO), 87.1 (Cp), 63.4 (OCH$_2$), 60.6 (Fe–C), 19.6 (CH$_2$), 15.9 ppm (CH$_3$); mass spectrum, *m/e* 262 (M$^+$), 234 (−CO), 206 (−2CO), 186 (Cp$_2$Fe$^+$). Anal. Calcd for $C_{12}H_{14}FeO_3$: C, 54.98; H, 5.39. Found: C, 54.84; H, 5.42.

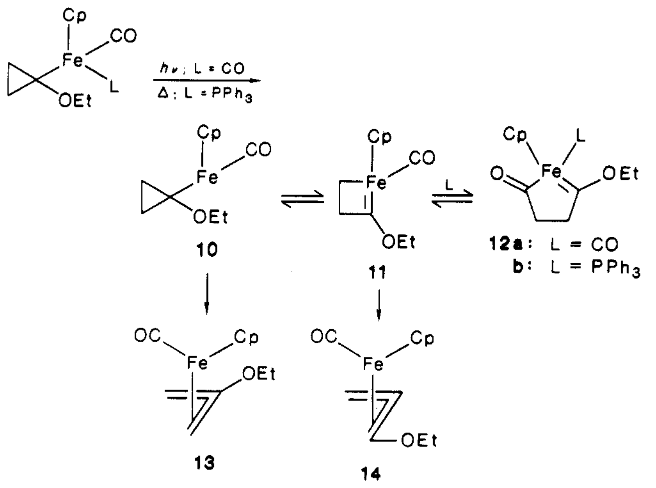
Compound **9b**: mp 97–99 °C; IR (C_6D_6) 1911 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6) 7.6–6.9 (m, 15 H, PPh$_3$), 4.36 (d, 5 H, J^4_{PH} = 1.5 Hz, Cp), 3.20 (m, 2 H, OCH$_2$), 1.00 (t, 3 H, CH$_3$), 0.54–0.21 ppm (m, 4 H, CH$_2$); ^{13}C NMR (50 MHz, C_6D_6) 222.4 (d, J^2_{PC} = 34.2 Hz, M–CO), 137.6 (d, J^1_{PC} = 39.1 Hz, C$_i$), 133.4 (d, J^3_{PC} = 9.8 Hz, C$_m$), 131.4 (d, J^4_{PC} = 7.4 Hz, C$_p$), 127.6 (d, J^2_{PC} = 9.8 Hz, C$_o$), 85.4 (Cp), 60.9 (OCH$_2$), 53.7 (d, J^1_{PC} = 29.3 Hz, C–OEt), 20.1, 17.9 (CH$_2$), 16.2 ppm (CH$_3$); chemical mass spectrum, *m/e* 497 (MH$^+$), 498 (−CO), 383 (CpFePPh$_3^+$), 234 (−PPh$_3$), 206 (−PPh$_3$, −CO), 186 (Cp$_2$Fe$^+$). Anal. Calcd for $C_{29}H_{29}FeO_2P$: C, 70.17; H, 5.89. Found: C, 69.34; H, 5.73.

Compound **12a**: mp 71–72 °C; IR (CCl$_4$) 1950, 1646 cm^{-1}; ^{1}H NMR (60 MHz, C_6D_6) 4.5 (s, 5 H, Cp), 4.0 (q, 2 H, OCH$_2$), 2.3 (m, 4 H, CH$_2$), 1.1 ppm (t, 3 H, CH$_3$); ^{13}C NMR (75 MHz, C_6D_6) 342.0 (M═C), 270.0 (M(CO)R), 216.9 (M–CO), 87.5 (Cp), 74.8 (OCH$_2$), 53.1, 49.3 (CH$_2$), 14.8 ppm (CH$_3$); mass spectrum, *m/e* 262 (M$^+$), 234 (−CO), 206 (−2CO), 186 (Cp$_2$Fe$^+$) 177 (Fp$^+$), 149 (CpFeCO$^+$), 121 (CpFe$^+$). Anal. Calcd for $C_{12}H_{14}FeO_3$: C, 54.98; H, 5.39. Found: C, 54.96; H, 5.43.

Compound **12b**: mp 148–149 °C; IR (C_6D_6) 1615 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6) 7.6–6.9 (m, 15 H, PPh$_3$), 4.48 (d, 5 H, J^4_{PH} = 1.35 Hz, Cp), 4.10 (m, 2 H, OCH$_2$), 2.10 (m, 4 H, CH$_2$), 1.06 ppm (t, 3 H, CH$_3$); ^{13}C NMR (75 MHz, C_6D_6) 341.0 (M═C), 293.3 (M(CO)R), 138.4–128.3 (PPh$_3$), 71.2 (OCH$_2$), 50.7, 49.2 (CH$_2$), 15.3 ppm (CH$_3$); mass spectrum, *m/e* 262 (PPh$_3^+$), 234 (−PPh$_3$), 186 (Cp$_2$Fe), 121 (CpFe$^+$). Anal. Calcd for $C_{29}H_{29}FeO_2P$: C, 70.17; H, 5.89. Found: C, 69.98; H, 5.91.

(5) Compound **11**: ^{13}C NMR (75 Mhz, C_6D_6) 335.0 (M═C), 224.0 (CO), 82.8 (Cp), 79.4 (OCH$_2$), 61.6, 56.8 (CH$_2$), 12.5 (CH$_3$); ^{1}H NMR (60 MHz, C_6D_6) 4.3 (s, Cp), 4.0 (m, OCH$_2$), 2.5–1.7 (m, CH$_2$), 0.9 ppm (t, CH$_3$).

Scheme II



column chromatography of this mixture yielded two yellow solids which, as a result of complete characterization[6] and comparison with known methoxy analogues,[7] are assigned the π-allyl structures **13** and **14**.

A reasonable mechanism for the origin of these two materials is provided in Scheme II. Consistent with this scheme is the well-established tendency of cyclopropanes to ring open when σ bonded to 16-electron metal systems[8] and the finding that each π complex is stable to the photochemical conditions of the reaction; i.e. one does not originate from the other. Rosenblum[7] found the corresponding methoxy-substituted π-allyl complexes to be photochemically stable. Furthermore, it was found that the relative amounts of the two π-allyl complexes were sensitive to both the source of their progenitors and to the presence of added CO. Thus, photolysis of pure acyl complex **12** led to relatively more of the terminal π-allyl complex than did photolysis of the σ-complex **9a** while photolysis of **9a** in the presence of added CO led to relatively more of the centrally substituted π-allyl complex than in its absence. Both of these observations are consistent with the ferracyclobutene as the progenitor to **14**,[9,10] if contraction of **11** to **10** is slow relative to ring opening and ring opening of **11** is slow relative to its reaction with CO.

Regardless of whether the metallacyclobutene goes directly to the terminal π-allyl complex, the above results are significant because they demonstrate quite conclusively the reversibility of both the α-elimination reaction (**10** to **11**) and the carbonyl insertion reaction (**11** to **12**). Additional evidence for this was obtained from the photolysis of **12a**. In addition to the π-allyl complexes, a small amount of the σ-complex **9a** was found in the product mixture.

Scheme II leaves unanswered a rather intriguing question: why does an electron-donating group appear to be required for the ring opening of **10** to **13**? At least two possibilities come to mind. One is the relatively trivial case in which chelation of the alkoxy oxygen[11] permits CO to escape from the solvent cage which, in effect, simply increases the quantum yield of the reaction by reducing back-reaction of the 16-electron intermediate with CO.[12] Pertinent to this, it is interesting that the unsubstituted cyclopropyl σ complex is inert to photolysis, even in THF. A second possibility is that the electron-donating group actually accelerates the ring opening by assisting the carbon–iron bond-breaking process. The viability of this possibility will depend on the detailed mechanism of the cyclopropyl ligand's ring opening, a question that we find most intriguing and are currently actively exploring.

In summary, we have found evidence for the thermal and reversible α-elimination of an alkyl group to produce a ferracyclobutene carbene complex. We believe that, in addition to contraction to the cyclopropyl complex **10**, the chemistry of this metallocyclobutene also includes migratory CO insertion to form a metallcyclic acylcarbene

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[6] Compound **13**: mp 130–132 °C; IR (CCl_4) 1945 cm^{-1}; ^{1}H NMR (100 MHz, C_6D_6) 4.27 (s, 5 H, Cp), 3.37 (q, 2 H, *J* = 6.9 Hz, OCH^2), 3.12 (d, 2 H, $J_{H_sH_a}$ = 1.2 Hz, Hs), 1.06 (t, 3 H, *J* = 6.9 Hz, CH_3), 0.69 ppm (d, 2 H, $J_{H_sH_a}$ = 1.2 Hz, H_a); ^{13}C NMR (25 MHz, C_6D_6) 221.3 (M–CO), 133.8 (C–OEt), 79.8 (Cp), 62.7 (OCH_2), 23.5 (CH_2), 14.7 ppm (CH_3); mass spectrum, *m/e* (M^+), 206 (–CO), 186 (Cp_2Fe^+), 121 ($CpFe^+$); high resolution calcd for $C_{11}H_{14}FeO_2$ 234.034 28, found 234.036 114, deviation +7.8 ppm.

Compound **14**: mp 128–129 °C; IR (CCl_4) 1940 cm^{-1}; ^{1}H NMR (100 MHz, C_6D_6) 4.49 (m, 1 H, Hc), 4.26 (s, 5 H, Cp), 3.83 (d, 1 H, $J_{H_cH_a}$ = 7.8 Hz, $H_a{}'$), 3.48 (q, 2 H, *J* = 7.2 Hz, OCH_2), 2.41 (dd, 1 H, $J_{H_sH_c}$ = 7.5 Hz, $J_{H_sH_a}$ = 2.1 Hz, H_s), 1.16 (t, 3 H, *J* = 7.1 Hz, CH_3), 0.33 ppm (dd, 1 H, $J_{H_aH_c}$ = 10.9 Hz, $J_{H_sH_a}$ = 2.1 Hz, H_a); ^{13}C NMR (25 MHz, C_6D_6) 222.2 (M–CO), 99.9 (C–OEt), 79.8 (Cp), 67.8 (OCH_2), 61.0 (CH), 22.4 (CH_2), 15.1 ppm (CH_3); mass spectrum, *m/e* 234 (M^+), 206 (–CO), 186 (Cp_2Fe^+), 177 (Fp^+), 149 ($CpFeCO^+$), 121 ($CpFe^+$), high resolution calcd for $C_{11}H_{14}FeO_2$ 234.034 28, found 234.034 96, deviation +2.9 ppm.

[7] On the basis Rosenblum's elegant work on the methoxy π-allyl complex corresponding to **14**, we feel that the syn (OEt cis to H) assignment of the latter is not only secure but that this is the kinetic product (Fish, R. W.; Giering W. P.; Marten, D.; Rosenblum M. *J. Organomet. Chem.* **1976**, *105*, 101–118).

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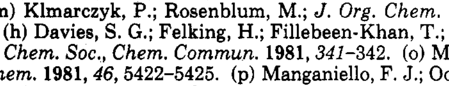
[9] The key step in rearrangement of the ferracyclobutene is hydrogen migration from the beta carbon to the carbene center to give a π complex (which is simply one end of the π-allyl). This is a well-known reaction of cationic, noncyclic iron carbene complexes [(a) LaCroce, S. J.; Menard, K. P.; Cutler, A. R. *J. Organomet. Chem.* **1980**, *190*, C79–C83. (b) Weinber, E. L.; Burton, J. T.; Baird, M. C.; Heberhold, Z. *Z. Natursforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 485–487. (c) Rosenblum, M.; Cutler, A.; Fish, R. W.; Giering, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 4354–4355. (d) Brown, D. *Prog. Inorg. Chem.* **1980**, *27*, 1. (e) Casey, C. P. *Reactive Intermediates*; Wiley: New York, 1981; Vol. 2, Chapter 3. (f) Fischer, E. O. *The Synthesis of Carbene Complexes*; Verlag: Weinheim, FRG, 1983. (g) Bly, R. S.; Silverman, G. S.; *Organometallics* **1984**, *3*, 1765–1767. (h) Kremer, K. A. M.; Kuo, G.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6110–6121. (i) Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1862–1864. (j) Kuo, G. *Organometallics* **1984**, *3*, 806–808. (k) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258–264. (l) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979–981. (m) Klmarczyk, P.; Rosenblum, M.; *J. Org. Chem.* **1978**, *43*, 3488–3493. (h) Davies, S. G.; Felking, H.; Fillebeen-Khan, T.; Tadj, F.; Watts, O. *J. Chem. Soc., Chem. Commun.* **1981**, *341*–342. (o) Marten, D. F. *J. Org. Chem.* **1981**, *46*, 5422–5425. (p) Manganiello, F. J.; Oon, S. M.; Radcliffe, M. D.; Jones, W. M. *Organometallics* **1985**, *4*, 1069–1072].

[10] An alternate mechanism for formation of **14** is by the following reaction sequence.



However, we do not consider this to be highly likely because cyclopropylmetal complexes tend to resist β-eliminations, presumably due to strain (ref 7b and unreported results from these laboratories).

[11] Chemistry analogous to the conversion of **9a** to **13a** has been observed when the ethoxy substituent is replaced by thiophenyl. However, in this case an intermediate with a molecular formula corresponding to a chelate has actually been isolated. The results of this work will be reported in a future publication.

[12] Very little ^{13}CO was incorporated (<1% as determined by ^{13}C NMR and mass spectrometric analyses) into the reisolated starting σ complex when the reaction was run in the presence of labeled carbon monoxide.

complex and rearrangement to a π-allyl complex. The detailed mechanism of these rearrangements as well as the chemistry of other substituted Fp-cyclopropyl complexes is currently under investigation.

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Regioselective Chelate Assisted Carbon-Halogen Oxidative Addition at Tungsten(0)

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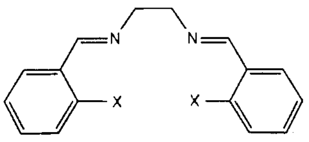
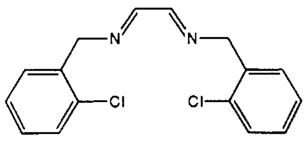
Summary: Regioselective aromatic carbon-halogen oxidative addition is observed in unsymmetrically substituted chelating ligands derived from 1,2-diaminobenzene. Aromatic carbon-chloride bonds on an imine arm of the ligand are cleaved in the presence of aromatic carbon-iodine bonds on a saturated arm. Crystallographic and vibrational analyses show that hydrogen bonding is important in the structure of the seven-coordinate tungsten(II) metallacycle product.

An important mode of activation and potential catalytic functionalization of carbon-heteroatom bonds is by oxidative addition to a low-valent metal.[1] Recently we reported that cleavage of aromatic carbon-halogen bonds in suitably designed ligands (1, X = Cl, Br, I) takes place readily at tungsten(0).[2] Interestingly, oxidative addition was not observed for the closely related conjugated ligand system 2. The basis for the diverse reactivity observed for chelates 1 and 2 may be a result of differing metal basicity[3] rather than ligand structure. In order to probe the role of the ligand in promoting these reactions, we have prepared several unsymmetrical ligands to compare the reactivity of saturated versus unsaturated pendant aryl halides to oxidative addition at an identical metal center. Mechanistic understanding of this type of reaction is important in the design of ligands for specific bond activation reactions at metal centers.[4]



1



2

Reduction of the 1:1 Schiff base 3 prepared from 1,2-diaminobenzene and a substituted benzaldehyde followed by treatment with 1 equiv of 2,6-dichlorobenzaldehyde affords 4a and 4b in approximately 70% yield (see Scheme I).[6] Treatment of 4 with $W(CO)_3(EtCN)_3$[5] in dichloromethane at room temperature for 2 h yields reddish orange solutions of 5a and 5b which can be isolated as orange crystalline solids in 70% and 63% yields, respectively.

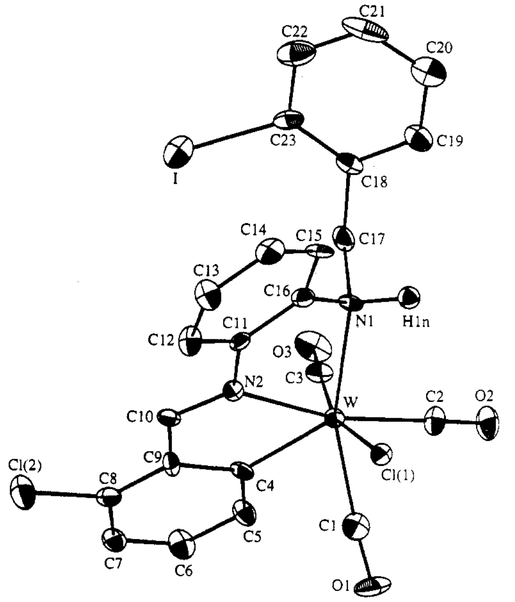
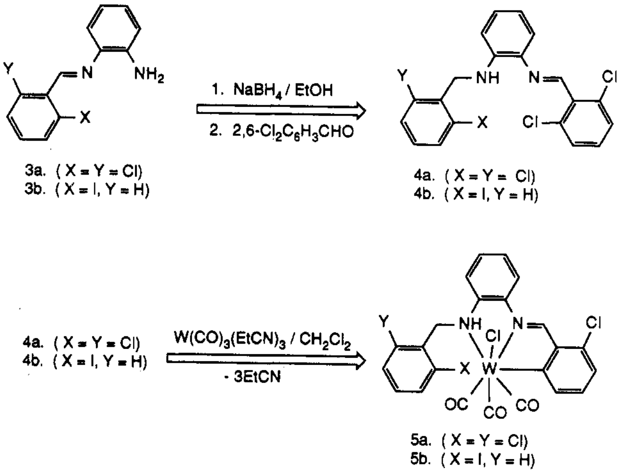


Figure 1. ORTEP representation of **5b**. Selected bond distances (Å) are as follows: W–C4, 2.20 (1); W–Cl(1), 2.536 (1); W–N1, 2.314 (7); W–N2, 2.154 (8); W–Cl, 2.03 (1); W–C2, 2.01 (1); W–C3, 1.97 (1). Selected bond angles (deg) are as follows: N1–W–Cl(1), 79.3 (2); N2–W–Cl(1), 84.1 (2); C4–W–Cl(1), 125.7 (2); N1–W–Cl, 155.3 (4); N2–W–C2, 167.7 (4); Cl(1)–W–C3, 165.6 (3).

Scheme I



These compounds were characterized by elemental analysis and ^1H NMR and IR spectroscopic methods. In the case of 5a,[7] the imine proton at δ 9.953 exhibits distinct satellites ($^3J_{WH}$ = 8.4 Hz) due to coupling to ^{183}W. This coupling is diagnostic of metallacycle formation in structurally characterized complexes of related ligands.[2,4] A broad resonance at δ 5.78 assigned to the N–H group is coupled to the diastereotopic protons of the benzyl arm

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(5) Kubas, G. J. *Inorg. Chem.* **1983**, *22*, 692.

(6) Analytical data for **4a**: IR (mull, cm^{-1}) 3348 (ν_{NH}), 2477 (ν_{ND}); ^1H NMR ($CDCl_3$) δ 8.803 (s, 1 H, HC=N), 7.4–6.7 (m, 10 H, aromatic), 5.49 (br, 1 H, NH), 4.66 (s, 2 H, CH_2). Anal. Calcd for $C_{20}H_{14}N_2Cl_4$: C, 56.77; H, 3.10; N, 6.62. Found: C, 56.81; H, 3.28; N, 6.58. Spectral data for **4b**: IR (mull, cm^{-1}) 3377 (ν_{NH}); ^1H NMR ($CDCl_3$) δ 8.874 (s, 1 H, HC=N), 7.8–7.1 (m, 11 H, aromatic), 4.37 (br, 1 H, NH), 4.17 (d, ^3J = 2.7 Hz, 2 H, CH_2).

(7) Anal. Calcd for $C_{23}H_{14}N_2Cl_4O_3W$ (**5a**): C, 36.93; H, 1.89; N, 3.74. Found: C, 37.12; H, 2.13; C, 3.67.

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