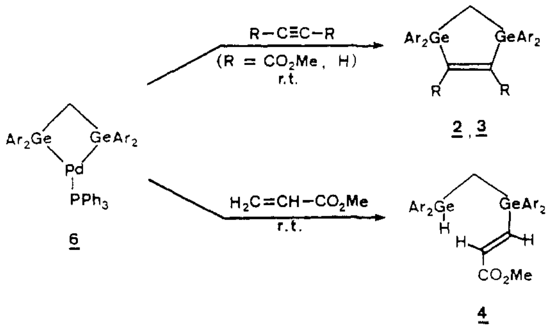
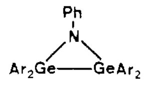
Scheme III

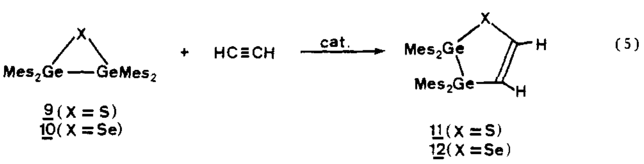


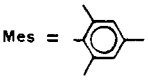
Under similar conditions azadigermiridine 8^{9c} did not react with dimethyl acetylenedicarboxylate or acetylene in the presence of $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$. But,



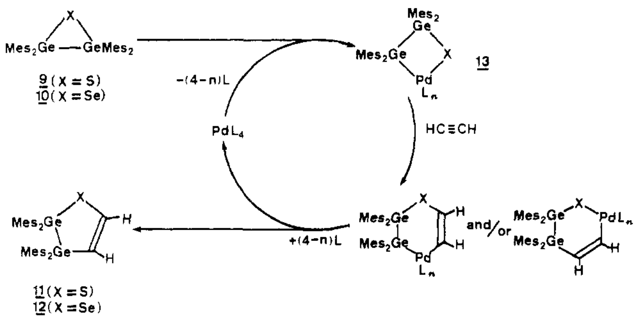
8

thiadigermirane $9^{9a,b}$ reacted with acetylene in the presence of a catalytic amount of $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ at 80 °C cleanly to produce the adduct 11^{19} in 44–54% yield (eq 5). In contrast to the reactions of digermirane 1 the adduct 11 obtained is the insertion product of acetylene into the Ge–S bond. No products of the insertion into the Ge–Ge bond were obtained. The reaction of selenadigermirane $10^{9a,b}$ with acetylene under similar conditions gave the corresponding addition product 12 (eq 5).[20] A simple catalytic scheme can be proposed for the formation of adducts 11 and 12 (Scheme IV). We tried to proof the intervention of an intermediate such as 13. However, attempts to isolate Pd-containing intermediates in stoichiometric reactions were not successful, so the chemistry in Scheme IV is only a suggestion.





Scheme IV



Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research (No. 63106003) from the Ministry of Education, Science, and Culture of Japan. We thank T. Kawai and Y. Nagai, Eisai Co., Ltd., for the X-ray analysis of compound 6.

Supplementary Material Available: Detailed information concerning IR, MS, and analytical data of new compounds (3 pages). Ordering information is given on any current masthead page.

---

[18] The mechanism of the palladium(II)-catalyzed insertions of acetylenes into the Ge–Ge bond of 1 is of some interest. As reported earlier (see ref 5) there is the possibility that a Pd(II) compound is reduced to a Pd(0) species. An experiment in which 1 was treated with a stoichiometric amount of $PdCl_2(PPh_3)_2$ confirmed that this was the case. The reaction produced two products, palladadigermetane and $ClAr_2Ge–CH_2–GeAr_2Cl$ (7), *in about a 1:1 ratio. It would appear that an initial* reaction of 1 with $PdCl_2(PPh_3)_2$ reduces the latter to $Pd(PPh_3)_2$ and forms 7. The coordinatively unsaturated $Pd(PPh_3)_2$ then inserts into the Ge–Ge bond of 1. Compound 7: colorless crystals, mp 119–121 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 24 H, CH_3), 2.51 (dq, J = 7.4, 14.8 Hz, 8 H, CH_2), 2.56 (s, 2 H, $GeCH_2Ge$), 2.77 (dq, J = 7.4, 14.8 Hz, 8 H, CH_2), 6.97 (d, J = 7.7 Hz, 8 H, Ar), 7.22 (t, J = 7.7 Hz, 4 H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.2 (q, CH_3), 28.0 (t, $GeCH_2Ge$), 29.1 (t, CH_2), 126.7 (d, Ar), 129.8 (d, Ar), 139.4 (s, Ar), 148.1 (s, Ar).

[19] Compound 11: colorless crystals; mp 174–175 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 2.10 (s, 12 H, CH_3), 2.21 (br s, 24 H, CH_3), 6.62 (br s, 8 H, Mes), 6.95 (AB, J_{AB} = 8.4 Hz, $\Delta\nu_{AB}$ = 30 Hz, 2 H, HC=CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8 (q, CH_3), 25.1 (q, CH_3), 25.2 (q, CH_3), 128.8 (d, Mes), 128.9 (d, Mes), 129.2 (d, C=C), 135.8 (s, Mes), 138.0 (s, Mes), 138.2 (s, Mes), 140.2 (d, C=C), 143.3 (s, Mes), 143.9 (s, Mes).

[20] Compound 12: colorless crystals, mp 114–120 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 2.13 (s, 12 H, CH_3), 2.21 (s, 24 H, CH_3), 6.63 (br s, 8 H, Mes), 7.41 (AB, J_{AB} = 10.2 Hz, $\Delta\nu_{AB}$ = 25.0 Hz, 2 H, CH=CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8 (q, CH_3), 20.9 (q, CH_3), 25.3 (q, CH_3), 25.5 (q, CH_3), 128.8 (d, Mes), 128.9 (d, Mes), 134.3 (d, C=C), 136.1 (s, Mes), 136.2 (d, C=C), 137.9 (s, Mes), 138.2 (s, Mes), 143.2 (s, Mes), 143.8 (s, Mes).

Inversion of Stereochemistry at the Carbon Bound to Iron in Cyclopropane Formation from *threo*-$C_5H_5(CO)_2FeCHDCHDCH_2S(CH_3)C_6H_5^+$

Charles P. Casey* and Laura J. Smith

McElvain Laboratory of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received June 5, 1989

Summary: Upon heating at 65 °C, *threo*-$C_5H_5(CO)_2FeCHDCHDCH_2S(CH_3)C_6H_5^+CF_3SO_3^-$ is converted to *cis*-1,2-dideuteriocyclopropane with inversion of stereochemistry at the carbon bound to iron.

The reaction of electrophilic carbene complexes with alkenes leads to the formation of cyclopropanes[1] with complete retention of alkene stereochemistry.[2] Since electron-rich alkenes have enhanced reactivity, electrophilic addition of the carbene carbon to the least substituted alkene carbon has been proposed to lead to a transition state with substantial positive charge at the carbon γ to the metal center. Cyclopropane formation can then be completed by carbon–carbon bond formation between C_α and C_γ by one of two stereochemically differentiated modes of ring closure (Scheme I). Net retention of stereochemistry at C_α could occur by nucleophilic attack of iron at the electrophilic γ-carbon to produce a cationic metallacyclobutane which then reductively eliminates cyclopropane.[3] Net inversion of stereochemistry at C_α could occur via a W-shaped transition state in which the electrophilic γ-carbon attacks the backside of the C_α–Fe bond.

---

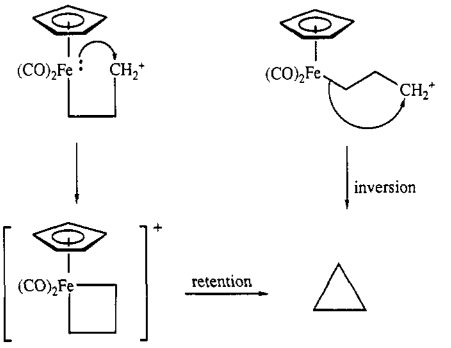
[1] Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.

[2] Alkene stereochemistry was partially lost in one case. Brookhart, M.; Kegley, S. E.; Husk, G. R. *Organometallics* **1984**, *3*, 650.

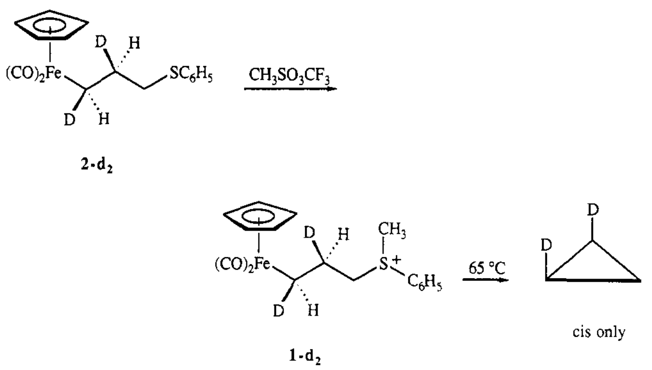
[3] (a) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149. (b) Hanks, T. W.; Jennings, P. W. *J. Am. Chem. Soc.* **1987**, *109*, 5023. (c) Al-Essa, R. J.; Puddephatt, R. J.; Tipper, C. F. H.; Thompson, P. J. *J. Organomet. Chem.* **1978**, *157*, C40. (d) Irwin, W. J.; McQuillin, F. J. *Tetrahedron Lett.* **1968**, 1937. (e) Powell, K. G.; McQuillin, F. J. *Tetrahedron Lett.* **1971**, 3313. (f) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 4233.

0276-7333/89/2308-2288$01.50/0

Scheme I



Scheme II



Inversion of stereochemistry at a carbon bound to a metal in cyclopropane formation has been seen previously in the solvolysis of 1,3-tin mesylates and related compounds.[4]

In an attempt to model the transition state for cyclopropane formation from metal carbene complexes, we studied the reaction of $C_5H_5(CO)_2Fe(CH_2)_3Br$ with Ag^+ and found that generation of an electrophilic center γ to iron led to cyclopropane formation.[5] Here we report that thermolysis of $C_5H_5(CO)_2Fe(CH_2)_3S(CH_3)C_6H_5^+$ (**1**) also leads to cyclopropane formation. In addition, use of stereochemically labeled sulfonium salts establishes that cyclopropane formation occurs with inversion of stereochemistry at the carbon bound to iron.[6]

$C_5H_5(CO)_2Fe(CH_2)_3SC_6H_5$ (**2**)[7] was prepared from the reaction of $Na^+[C_5H_5(CO)_2Fe]^-$ (2.3 mmol) with $(p\text{-}CH_3C_6H_4)SO_3(CH_2)_3SC_6H_5$ (**3**)[8] (1.9 mmol) in THF at 0 °C. Iron sulfide **2** was isolated in 63% yield as a dark yellow, low melting oil (mp 15–20 °C). Methylation of **2** (3 mmol) with 1 equiv of $CF_3SO_3CH_3$ in CH_2Cl_2 at room temperature produced the sulfonium salt $C_5H_5(CO)_2Fe(CH_2)_3S(CH_3)C_6H_5^+CF_3SO_3^-$ (**1**-CF_3SO_3) as a thick red oil in 35% isolated yield.[9]

The neat triflate salt **1**-CF_3SO_3 was generated in situ from the reaction of **2** with 0.95 equiv of $CF_3SO_3CH_3$ and heated to 65 °C to generate cyclopropane in 62% yield.[10] Similarly, **1**-CF_3SO_3 generated in situ in CH_2Cl_2 gave cyclopropane upon heating at 65 °C.

To determine the stereochemistry of cyclopropane formation, we synthesized stereospecifically labeled *threo*-$C_5H_5(CO)_2FeCHDCHDCH_2SC_6H_5$ (**2**-d_2). Reduction of acetylene-d_2 with chromous chloride produced pure *trans*-1,2-dideuterioethylene[11] containing no infrared-detectable[12] *cis*-CHD=CHD or $CHD{=}CH_2$. Reaction of the *trans*-CHD=CHD with bromine in water gave the *erythro*-bromohydrin, BrCHDCHDOH,[13] which was cyclized with 1 M NaOH to *trans*-1,2-dideuteriooxirane (**4**)[14] in 41% yield (23% from ethylene). Epoxide **4** was opened with ((phenylthio)methyl)lithium to give *erythro*-$HOCHDCHDCH_2SC_6H_5$ (**5**)[15] in 57% yield. Alcohol **5** was converted to the tosylate **3**-d_2[16] with tosyl chloride in pyridine (92%). Finally, reaction of tosylate **3**-d_2 with the $Na^+[C_5H_5(CO)_2Fe]^-$ gave *threo*-**2**-d_2[17,18] which was purified by column chromatography (82%).

Reaction of the labeled iron sulfide *threo*-**2**-d_2 (120 mg; 0.36 mmol) with neat methyl triflate (0.32 mmol) followed by thermolysis of the sulfonium salt at 65 °C for 6 h produced *cis*-1,2-dideuteriocyclopropane in 45% yield as the only detectable volatile product (Scheme II). 1,2-Dideuteriocyclopropane was identified by ^1H NMR (δ 0.12) and GC/MS, which established that the product was greater than 97% d_2. The stereochemistry of the cyclopropane was shown to be cis by gas-phase infrared spectroscopy, which exhibited bands at 2279, 1038, and 846 cm^{-1} that are characteristic of *cis*-1,2-dideuteriocyclo-

---

(4) (a) Kuivila, H. G.; Scarpa, N. M. *J. Am. Chem. Soc.* **1970**, *92*, 6990. (b) Davis, D. D.; Chambers, R. L.; Johnson, H. T. *J. Organomet. Chem.* **1970**, *25*, C13. (c) Davis, D. D.; Black, R. H. *J. Organomet. Chem.* **1974**, *82*, C30. (d) Davis, D. D.; Johnson, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7576. (e) McWilliam, D. C.; Balasubramanian, T. R.; Kuivila, H. G. *J. Am. Chem. Soc.* **1978**, *100*, 6407. (f) Fleming, I.; Urch, C. J. *Tetrahedron Lett.* **1983**, *24*, 4591. (g) Fleming, I.; Urch, C. J. *J. Organomet. Chem.* **1985**, *285*, 173. (h) Kadow, J. F.; Johnson, C. R. *Tetrahedron Lett.* **1984**, *25*, 5255. (i) Peterson, D. J.; Robbins, M. D. *Tetrahedron Lett.* **1972**, 2135. (j) Peterson, D. J.; Robbins, M. D.; Hansen, J. R. *J. Organomet. Chem.* **1974**, *73*, 237.

(5) Casey, C. P.; Smith, L. J. *Organometallics* **1988**, *7*, 2419.

(6) Brookhart has found inversion of stereochemistry at the carbon bound to iron of $C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$ in cyclopropane formation and has informed us of his results prior to publication. Brookhart, M.; Liu, Y. *Organometallics* **1989**, *8*, 1569.

(7) For **2**: ^1H NMR (200 MHz, acetone-d_6) δ 7.33–7.11 (m, C_6H_5), 4.90 (s, C_5H_5), 2.92 (t, J = 7 Hz, CH_2S), 1.75 (m, CH_2), 1.45 (m, $FeCH_2$); $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6) δ 218.7 (CO), 138.4 (C_{ipso}), 129.6, 128.8 ($C_{ortho,meta}$), 125.9 (C_{para}), 86.5 (C_5H_5), 38.2 (CH_2), 37.1 (CH_2S), 1.95 ($FeCH_2$); IR (hexane) 2011 (s), 1957 (s), 1927 (w) cm^{-1}; HRMS calcd for $(M - 2CO)^+$, $C_{14}H_{16}FeS$ 272.0322, found 272.0316.

(8) (a) Nambara, T.; Matsuhisa, N. *Yakugaku Zasshi* **1963**, *83*, 642 (*Chem. Abstr.* **1963**, *59*, 7411f). (b) Fong, H. O.; Hardstaff, W. R.; Kay, D. G.; Langler, R. F.; Morse, R. H.; Sandoval, D. N. *Can. J. Chem.* **1979**, *57*, 1206.

(9) For **1**-CF_3SO_3: ^1H NMR (500 MHz, acetone-d_6) δ 8.20–7.73 (m, C_6H_5), 4.92 (s, C_5H_5), 3.20 (m, CH_2S), 3.47 (s, CH_3), 1.82 (m, CH_2), 1.40 (m, $FeCH_2$); $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6) δ 218.9 (CO), 138.1 (C_{ipso}), 132.2, 129.0 ($C_{ortho,meta}$), 124.1 (C_{para}), 86.7 (C_5H_5), 49.5 (CH_2S), 32.3 (CH_2), 26.4 (CH_3), −1.0 ($FeCH_2$); IR (hexane) 2005 (w), 2001 (s), 1950 (s) cm^{-1}.

(10) Cyclopropane was identified by ^1H NMR (δ 0.13 in C_6D_6), IR (gas: 3100, 3022, 1027, 866 cm^{-1}), and GC/MS.

(11) (a) Nicholas, P. P.; Carroll, R. T. *J. Org. Chem.* **1968**, *33*, 2345. (b) Price, C. P.; Spector, R. *J. Am. Chem. Soc.* **1966**, *88*, 4171.

(12) Major IR bands for *trans*-CHD=CHD[11a] appear at 1298, 987, and 727 cm^{-1}, for *cis*-CHD=CHD[11a] at 1342 and 842 cm^{-1}, and for $CHD{=}CH_2$ at 1402, 1000, 943, and 808 cm^{-1}. Brondsema, P. Ph.D. Dissertation, University of Wisconsin—Madison, 1984.

(13) The procedure of Price[11b] was modified as suggested by Brookhart: 150 mL of a 0.19 M solution of bromine in water was added to 0.02 mol of *trans*-CHD=CHD at room temperature.

(14) For **4**: ^1H NMR (200 MHz, C_6D_6) δ 0.54; IR (gas) 3023, 2241, 1742, 1227, 1110, 916, 889, 878, 817, 750 cm^{-1}.

(15) For **5**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.36–7.10 (m, C_6H_5), 3.68 (br d, J = 6 Hz, CHDO), 2.97 (br d, J = 8 Hz, CH_2S), 1.80 (br q, J = 8 Hz, CHD), 1.50 (br s, OH); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 136.2 (C_{ipso}), 129.1, 128.9 ($C_{ortho,meta}$), 125.9 (C_{para}), 60.9 (t, J_{CD} = 21 Hz, CHDO), 31.2 (t, J_{CD} = 19 Hz, CHD), 30.1 (CH_2S); IR (film) 3352, 2922 cm^{-1}; HRMS calcd for $C_9H_{10}D_2OS$ 170.0734, found 170.0730.

(16) For **3**-d_2: ^1H NMR (200 MHz, $CDCl_3$) δ 7.8–7.7, 7.4–7.2 (C_6H_5, C_6H_4), 4.13 (br d, J = 6 Hz, CHDO), 2.91 (br d, J = 8 Hz, CH_2S), 2.44 (s, CH_3), 1.90 (br q, J = 8 Hz, CHD); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.8, 135.4, 133.0, 129.8, 129.6, 129.0, 127.8, 126.3 (C_{aryl}), 68.2 (t, J_{CD} = 23 Hz, CHDO), 29.6 (CH_2S), 28.0 (t, J_{CD} = 20 Hz, CHD), 21.6 (CH_3); IR (film) 3062, 2925, 1363, 1180 cm^{-1}; HRMS calcd for $C_{16}H_{16}D_2O_3S_2$ 324.0822, found 324.0823.

(17) For **2**-d_2: ^1H NMR (200 MHz, acetone-d_6) δ 7.32–7.14 (m, C_6H_5), 4.91 (s, C_5H_5), 2.91 (br d, J = 6 Hz, CH_2S), 1.73 (m, CHD), 1.43 (m, FeCHD); $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6) δ 218.8 (CO), 138.5 (C_{ipso}), 129.6, 128.9 ($C_{ortho,meta}$), 126.0 (C_{para}), 86.6 (C_5H_5), 37.8 (t, J_{CD} = 18 Hz, CHD), 37.1 (CH_2S), 1.54 (t, J_{CD} = 19 Hz, FeCHD); IR (hexane) 2010 (s), 1967 (s) cm^{-1}.

(18) Similar reactions occur with clean inversion of stereochemistry at carbon: (a) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814. (b) Whitesides, G. M.; Boschetto, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 1529.

propane. Bands corresponding to the trans isomer at 2271, 1024, 1041, and 849 cm^{-1} were absent.[19] This result demonstrates that cyclopropane formation occurs with inversion of stereochemistry at the carbon bound to iron. This result supports a mechanism involving backside attack of the electrophilic γ-carbon at the iron–carbon bond through a W-shaped intermediate and is inconsistent with a mechanism involving a metallacyclobutane intermediate.

Earlier we had attempted to explain the formation of cis cyclopropanes from $(CO)_5W{=}CHPh$ and *cis*-$CH_3HC{=}CHCH_3$ or $(CH_3)_2C{=}CHCH_3$ by a mechanism involving interaction of the ipso carbon of the aryl ring on C_α with the more substituted alkene carbon followed by conversion to a metallacycle and reductive elimination.[20] The results here demonstrating inversion of stereochemistry at the α-carbon strongly suggest that this explanation is incorrect. Since this constitutes our second retraction of explanations for the stereochemistry of the product cyclopropanes, we are reluctant to offer a third at this time.

Acknowledgment. We wish to thank Maurice Brookhart for informing us of his related work prior to publication and Jerome Berson for providing IR spectra of *cis*- and *trans*-dideuteriocyclopropane. Financial support from the National Science Foundation is gratefully acknowledged.

Registry No. **1**-CF_3SO_3, 122171-43-1; **1**-d_2, 122171-48-6; **2**, 122171-44-2; **2**-d_2, 122171-46-4; **3**, 71350-90-8; **3**-d_2, 122171-41-9; **4**, 13482-13-8; **5**, 122171-40-8; $Na^+[C_5H_5(CO)_2Fe]^-$, 122171-45-3; (*R**,*S**)-BrCHDCHDOH, 80236-19-7; cyclopropane, 75-19-4; acetylene-d_2, 1070-74-2; *trans*-1,2-dideuterioethylene, 1517-53-9; ((phenylthio)methyl)lithium, 13307-75-0; *cis*-1,2-dideuteriocyclopropane, 122211-66-9.

---

(19) (a) Pedersen, L. D. Ph.D. Dissertation, Yale University, 1975. (b) Berson, J. A.; Pedersen, L. D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1976**, *98*, 122.

(20) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

Reactions of Chloro((tri-2,4,6-*tert*-butylphenyl)imino)phosphane with Anionic Transition-Metal Complexes: Stable Metalloiminophosphanes and Evidence for Terminal Aminophosphinidene Complexes

Edgar Niecke,* Joachim Hein, and Martin Nieger

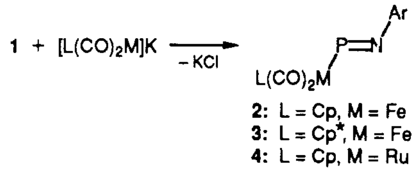
Anorganisch-Chemisches Institut der Universität Bonn
Gerhard-Domagk-Strasse 1, D-5300 Bonn 1, FRG

Received April 10, 1989

Summary: Reaction of $[(Cl)P{=}N(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)]$ (**1**) with $[(\eta^5\text{-}Me_5C_5)(CO)_2Fe]K$ affords the stable metalloiminophosphane $[(\eta^5\text{-}Me_5C_5)(CO)_2FeP{=}N(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)]$ (**3**), the structure of which was determined by X-ray crystallography. Rearrangement of the tungsten compound $[(\eta^5\text{-}Me_5C_5)_2W(H)(PN(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)]$ (**6**) via a 1,3-hydrogen shift results in the formation of the terminal aminophosphinidene complex $[(\eta^5\text{-}Me_5C_5)_2WPN(H)(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)]$ (**7**), identified spectroscopically.

A variety of iminophosphane complexes is known,[1] demonstrating the versatility of phosphorus–element pπ systems as ligands. So far only η^1-coordination to one metal fragment has been observed with the iminophosphane acting as a two-electron donor via the lone pair at the phosphorus atom. However, organometal-substituted iminophosphanes of the type $L_nMP{=}NR$, i.e. the P=N moiety acting as one-electron donor, have so far only been postulated as intermediates[2] or could only be detected spectroscopically due to decomposition at room temperature as for $L_nM = (R_3P)(CO)Ni$.[3] Here, we report on the first stable metalloiminophosphanes, $L(CO)_2MP{=}NAr$ (L = Cp (η^5-C_5H_5), M = Fe, Ru; L = Cp* (η^5-C_5Me_5), M = Fe; Ar = 2,4,6-*t*-$Bu_3C_6H_2$), the synthesis of which had been prompted by the recent discovery of the chloroiminophosphane **1**.[4] This concept is analogous to the preparation of $[Cp^*(CO)_2FeP{=}C(SiMe_3)_2]$[5] from $[ClP{=}C(SiMe_3)_2]$, and thus, after phosphavinyl complexes and metallodiphosphenes,[6] organometal-substituted iminophosphanes have become accessible.

Scheme I



In a typical preparation a pentane solution of **1** (1.63 g, 5 mmol) was added to a solution of an equimolar quantity of $[Cp^*(CO)_2Fe]K$ in tetrahydrofuran at 0 °C. After being warmed to room temperature, the dark brown reaction mixture was stirred for 15 h and filtered and the filtrate evaporated to dryness. Recrystallization from petroleum ether (bp 40–60 °C) at –30 °C afforded dark brown **3**.[7] [Attempts to prepare P-metalated iminophosphanes from anionic group VIB transition-metal complexes $[L(CO)_3M]M'$ (L = Cp, Cp*; M = Cr, Mo, W; M′ = Li, Na, K) failed so far due to the thermal instability of the resulting products. Only ^{31}P NMR spectroscopic evidence could be obtained for a tungsten compound assumed to be $[Cp^*(CO)_3WP{=}NAr]$ (δ = 754 ppm), which decomposes rapidly at temperatures above –40 °C.] The reactions with $[Cp(CO)_2Fe]K$ and $[Cp(CO)_2Ru]K$ were performed analogously and furnished products **2** and **4**, respectively. In the $^{31}P\{^1H\}$NMR spectra the signals for **2**, **3**, and **4** are found, as expected, at extremely low field, viz. δ = 717, 787, and 688 ppm (H_3PO_4 external, C_6D_6), respectively. These low-field shifts are accounted for by the organo-

---

(1) (a) Scherer, O. J.; Konrad, R.; Guggolz, E.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 297. (b) Scherer, O. J.; Kerth, J. Asselmann, R. Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 984. (c) Arif, A. M.; Cowley, A. H.; Pakulski, M. *J. Am. Chem. Soc.* **1985**, *107*, 2553.

(2) Gudat, D.; Niecke, E.; Krebs, B.; Dartmann, M. *Organometallics* **1986**, *5*, 2376.

(3) Gudat, D.; Niecke, E. *J. Chem. Soc., Chem. Commun.* **1987**, 10.

(4) Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1715.

(5) Gudat, D.; Niecke, E.; Arif, A. M.; Cowley, A. H.; Quashie, S. *Organometallics* **1986**, *5*, 593.

(6) Weber, L.; Reizig, K.; Bungardt, D.; Boese, R. *Organometallics* **1987**, *6*, 110.

(7) Data for compounds **2**, **3**, and **4**: MS (EI, 70 eV, *m/e* (relative intensity)); ^1H NMR (δ, C_6D_6); $^{13}C\{^1H\}$ (δ, C_6D_6); $^{31}P\{^1H\}$ (δ, C_6D_6); IR (cm^{-1}, pentane). **2**: IR 2037 s, 1983 s; MS 467 (<1, M^+), 346 (2, $M^+ - 2CO - Cp$); ^1H 1.4 (s, 18 H, *o*-tBu), 1.5 (s, 9 H, *p*-tBu), 4.4 (s, 5 H, C_5H_5), 7.6 (s (br), 2 H, C_6H_2); $^{13}C\{^1H\}$ 211.5 ($Fe(CO)_2$), 87.6 (d, *J* = 5 Hz, C_5H_5); $^{31}P\{^1H\}$ 717. **3**: IR 1998 s, 1953 s; MS 537 (M^+, 10), 481 (83, $M^+ - 2CO$); ^1H 1.1 (d(br), *J* = 3 Hz, 15 H, C_5Me_5), 1.2 (s, 9 H, *p*-tBu), 1.3 (s, 18 H, *o*-tBu), 7.3 (s (br), 2 H, $tBu_3C_6H_2$); $^{13}C\{^1H\}$ 213.6 ($Fe(CO)_2$), 154.8 (PNCCC*C*), 141.0 (PNC*C*), 129.9 (d, *J* = 30 Hz, PNC), 121.5 (PNCC*C*), 98.7 (*C*$_5$Me$_5$); 36.2, 34.7, 32.2 (CMe_3), 9.1 (d, *J* = 7 Hz, C$_5$*Me*$_5$). $^{31}P\{^1H\}$ 787. **4**: IR 2022 s, 1982 s; MS 513 (<1, M^+), 457 (<1, $M^+ - 2CO$); ^1H 1.5 (s, 18 H, *o*-tBu), 1.5 (s, 9 H, *p*-tBu), 4.7 (s, 5 H, C_5H_5), 7.6 (s, 2 H, C_6H_2); $^{13}C\{^1H\}$ 201.7 ($Ru(CO)_2$), 90.5 (d, *J* = 3 Hz, C_5H_5); $^{31}P\{^1H\}$ 688. The ^{13}C NMR data for the 2,4,6-*t*-$Bu_3C_6H_2$ groups of compounds **2** and **4** are very similar to those observed for **3**.

0276-7333/89/2308-2290$01.50/0