the central CH and the anti CH of an allylic group. Two other coupling constants, 7.09 and 7.65 Hz at δ 3.74 and 3.22 ppm, respectively, are assigned as the proton coupling between central and syn protons. In the ^{13}C NMR spectrum, coupling constants between W and all the allylic carbon atoms are in the range 3.8–7.1 Hz, indicating the η^3-allylic bonding mode. Since alcohol is not as strong a nucleophile as amine, addition of alcohol across the terminal double bond of the allenyl ligand does not take place. Instead, the reaction results in the formation of the allyl complex **5** with the ester group bound to the terminal carbon at the anti position of the allylic ligand.

Both complexes **3** and **4** are also identified on the basis of their single-crystal X-ray analysis.[8] The ORTEP drawing of **3** is shown in Figure 1. It is clear that the organic ligand of **3** is bonded to the metal in an η^2 fashion. The most interesting structural feature is this four-membered tungstacyclic ring, which includes the atoms W, C(10), C(8), and N(7). The C(10)–C(8) distance of 1.524 (11) Å and the C(8)–N(7) distance of 1.469 (9) Å are typical for single bonds. These distances are to be contrasted with the comparable ones in a aza manganacyclic system,[9] $(CO)_4Mn[C(=N\text{-}p\text{-tolyl})C(=N\text{-}p\text{-tolyl})CH_2C_6H_4\text{-}p\text{-OMe}]$, where there exists a C=N bond with C—C = 1.490 (5) Å and C=N = 1.287 (4) Å. The allyl ligand of **4** is coordinated symmetrically to the tungsten with two approximately equal C—C bonds (details given in the supplementary material). Unlike that of **3**, the distance between the central carbon and the metal, W–C(8), is 2.77 (2) Å, showing that there is now bonding.

Using tungsten propargyl and allenyl complexes, we have demonstrated the facile C–C bond formation and its regiospecific control by means of the different bonding types of the C_3 unit to the metal. Further work is in progress, and the details of the regiospecificity and stereochemistry of the C—C bond formation will be the subject of future reports.

Acknowledgment. This research has been supported by the National Science Council (NSC) of the Republic of China. The NMR instruments used were funded by the NSC Instrumentation Program.

Supplementary Material Available: Details of the structure determination for complexes **3** and **4**, including tables of crystal and data collection parameters, general temperature factor expressions (*B*'s), positional parameters and their estimated standard deviations, and intramolecular distances and angles, spectroscopic data for complexes **3**–**6**, and an ORTEP drawing of complex **4** (10 pages); tables of observed and calculated structure factors for **3** and **4** (18 pages). Ordering information is given on any current masthead page.

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[8] X-ray analysis of **3** and **4**. Crystal data for **4** are as follows: space group $P2_1/c$, a = 8.6963 (13) Å, b = 20.691 (4) Å, c = 9.1135 (22) Å, β = 108.81 (2)°, Z = 4. X-ray data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. A total of 2728 reflections were collected with use of the ω–2θ scanning technique between 2.0 and 49.8° in 2θ. A total of 1920 reflections with $I > 2\sigma(I)$ were used in the full-matrix least-squares refinement. The structure was solved by using heavy-atom methods with the NRCC computing package. The final values of the agreement indices were R = 0.030, R_w = 0.028, and GOF = 1.75. Crystal data for **3** are as follows: space group $C2/c$, a = 20.551 (8) Å, b = 11.100 (4) Å, c = 12.784 (3) Å, β = 94.40 (3)°, Z = 8. The final residuals refined against 1889 data for which $I > 2.0\sigma(I)$ were R = 0.031, R_w = 0.024, and GOF = 1.78.

[9] (a) Motz, P. L.; Alexander, J. J.; Ho, D. M. *Organometallics* **1989**, *8*, 2589. (b) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751. (c) Handwerker, B. M.; Garrett, K. E.; Nagle, K. L.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 1562.

X-ray Structure Analysis and Reactivity of the Zirconaazaphosphirane $Cp_2Zr(Cl)N(SiMe_3)P(H)N(SiMe_3)_2$

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Received September 17, 1990

Summary: The structure of the 18-electron complex $Cp_2Zr(Cl)N(SiMe_3)P(H)N(SiMe_3)_2$ (**3a**) has been determined by single-crystal X-ray diffraction. Reaction of **3a** with $MeOSO_2CF_3$ and $Me_3SiOSO_2CF_3$ leads, with ring retention, to the neutral and cationic zirconium phosphorus species **9** and **10**, respectively, while ring opening with formation of a phosphorus–iron complex or phosphorus sulfide or selenide occurs when **3a** is treated with $Fe_2(CO)_9$, S_8, or Se, respectively.

It is well-known that hydrozirconation of olefins with a zirconium hydride such as Cp_2ZrHCl (**1**) places the zirconium moiety at the sterically less hindered position of the olefin chain as a whole.[1] Nevertheless, it has also been reported that hydrozirconation of styrene gives both terminal and internal products.[2] Indeed, the reactions of Cp_2ZrHCl are very much akin to the reactions of dialkylboranes. The resulting products are emerging as useful reagents and intermediates for organic synthesis.

Surprisingly, no similar work has been undertaken with unsaturated, low-coordinated, heavier main-group-element species. Such reactions might lead to new kinds of met-

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[1] Reviews: Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. Negishi, E.; Takamashi, T. *Synthesis* **1988**, *1*, 1. Erker, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397.

[2] Nelson, J. E.; Bercaw, J. E.; Labinger, J. A. *Organometallics* **1989**, *8*, 2484.

0276-7333/91/2310-0045$02.50/0

Table I. Crystal Data for $C_{19}H_{38}Si_3N_2PClZr$ (3a)

formula	$C_{19}H_{38}Si_3N_2PClZr$
fw	536.4
space group	$P2_1/n$
a, Å	14.199 (2)
b, Å	9.819 (2)
c, Å	19.885 (3)
β, deg	95.80 (1)
V, Å^3	2758
Z	4
μ(Mo Kα), cm^{-1}	6.8
d_{calc}, g cm^{-3}	1.29
2θ range, deg	$3 < 2\theta < 50$
scan width, deg	$0.9 + 0.34 \tan\theta$
scan speed, deg min^{-1}	2.0 < speed < 10.1
diffractometer	Enraf-Nonius CAD4
no. of rflns collected	4995
no. of unique rflns	4847
merging R factor	0.012
no. of rflns with $I > 3\sigma(I)$	2930
abs cor	Difabs
R	0.0314
R_w	0.0328 (unit wt)
no. of variables	360

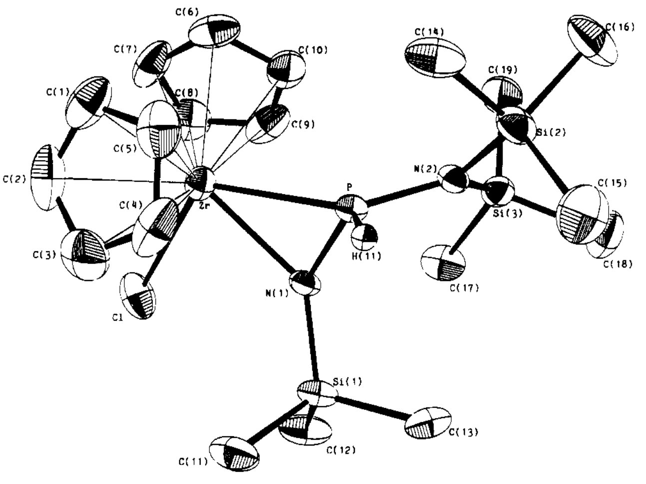
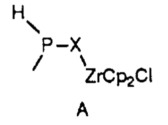
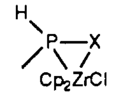


Figure 1. ORTEP drawing of **3a** showing the atomic numbering scheme.

alated group 13–15 compounds. We reasoned that reaction of the hydride **1** with dicoordinated phosphorus compounds might give either acyclic compounds of type A or metallacyclic compounds of type B. Our first experiments



A

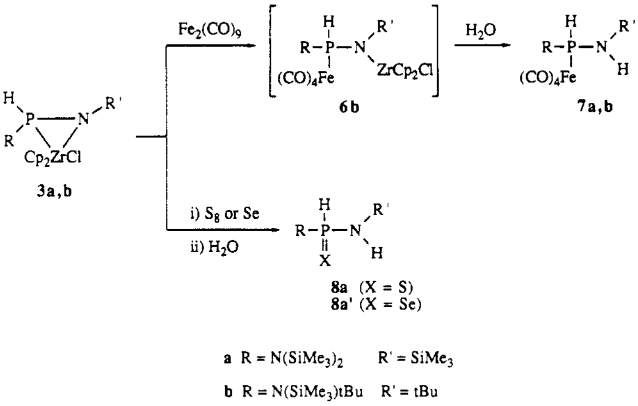


B

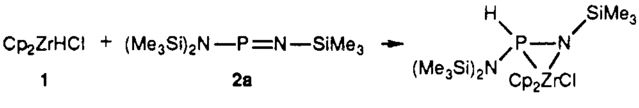
X = C<, N–, P–, etc.

in this field dealt with phosphorus derivatives such as phosphaalkenes (RP=C<) and phosphaimines (RP=N–).[3] We now report (i) the first X-ray structural determination of the zirconaazaphosphirane **3a** and (ii) some aspects of the reactivity of **3a**, including ring opening or ring retention with the formation of the first cyclic cationic phosphorus–zirconium species **10** and **11**. These cationic complexes are of great interest, since cationic d^0 metal alkyl complexes Cp_2MR^+ (M = Zr, Ti) have been recently implicated as catalysts in Ziegler–Natta olefin polymerization.[4]

Scheme I

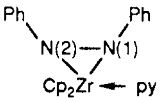


We have already reported[3] that **1** reacts with (bis(trimethylsilyl)amino)(trimethylsilylimino)phosphane (**2a**)[5] to give bis(cyclopentadienyl)chloro(trimethylsilyl)(bis(trimethylsilyl)amino)zirconaazaphosphirane (**3a**) in nearly quantitative yield.

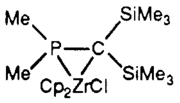


3a

A single-crystal X-ray structure analysis of **3a**[6] was carried out and the molecular structure is shown in Figure 1. The P and N(1) atoms are coordinated to the Cp_2ZrCl center, and the P, N(1), Zr, and Cl atoms are nearly coplanar as shown by the negligible displacement of the specific atoms from the plane (Zr, –0.003 Å; Cl, 0.003 Å; P, 0.004 Å; N, –0.004 Å). The Zr–N(1) distance (2.267 (3) Å) is longer than that in zirconium three-membered-ring compound **4**[7] (Zr–N(1) and Zr–N(2) = 2.105(4) and 2.161 (3) Å for **4**) but significantly shorter than Zr–N(3) in the same molecule (**4**: Zr–N(3) = 2.431 (4) Å, N(3) being the



4 (py = pyridine)



5

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(3) Majoral, J. P.; Dufour, N.; Meyer, F.; Caminade, A. M.; Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1990**, 507.

(4) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041. Jordan, R. F.; Lapointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892 and references therein.

(5) Niecke, E.; Flick, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *85*, 585. Scherer, O. J.; Kuhn, N. *J. Organomet. Chem.* **1974**, *82*, C3–C6.

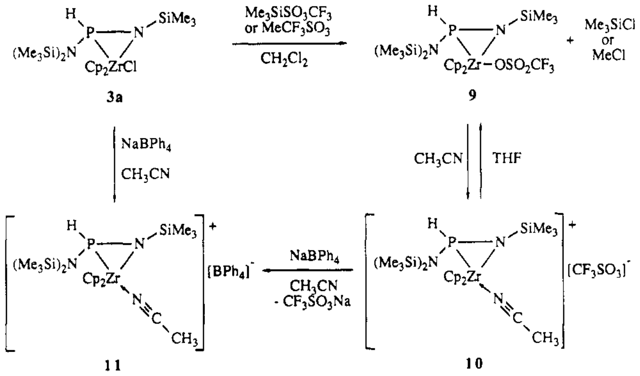
(6) Crystal data: A selected crystal was set up on an Enraf-Nonius CAD4F diffractometer. Accurate unit cell dimensions and crystal orientation matrices together with their estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 reflections. Two standard reflections were monitored periodically; at the end of data collection the crystal had decayed by about 28%. Corrections were made for Lorentz and polarization effects and for decay. Empirical absorption corrections were applied (Difabs).[13] Crystallographic data and other pertinent information are summarized in Table I. Computations were performed by using CRYSTALS,[14] adapted to a MicroVax II computer. Atomic form factors for neutral Zr, Cl, P, Si, C, N, and H atoms were taken from ref 15. Anomalous dispersion was taken into account. The structure was solved by interpretation of the Patterson maps, which clearly indicated Zr atom positions. All remaining nonhydrogen atoms were found by successive electron density map calculations. Their atomic coordinates were refined together with anisotropic temperature factors. At this stage, hydrogen atoms were located on a difference electron density map; their coordinates were refined with an overall isotropic temperature factor. Least-squares refinements with approximation to the normal matrix were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The models reached convergence with $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum_w(|F_o|^2)]^{1/2}$. The criteria for a satisfactory complete analysis were the ratios of the rms shift to standard deviation being less than 0.1 and no significant features in the final difference maps.

(7) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 894.

nitrogen atom of the pyridine ligand). The P-Zr (2.562 (1) Å) as well as the Zr–Cl (2.535 (2) Å) bonds are virtually identical with those in **5**.[8] (**5**: P-Zr = 2.606 (1) Å, Zr-Cl = 2.554 (1) Å). The endocyclic P-N(1) bond (1.609 (3) Å) is shorter than the exo bond (P-N(2) = 1.691 (3) Å), reflecting a very weak residual iminophosphorane character in **3a**. Noteworthy is the difference between the ZrN(1)P and ZrPN(1) angles (80.8 (1) and 60.9 (1)°, respectively), a consequence of quite different P-Zr and Zr-N bond lengths. Such a phenomenon is not observed in **5**, where the Zr-C and Zr-P distances are equal, or in **4**, where the two endocyclic Zr-N bond lengths are similar.

The reaction of $Fe_2(CO)_9$ with bis(cyclopentadienyl)chloro-*tert*-butyl((trimethylsilyl)-*tert*-butylamino)zirconaazaphosphirane (**3b**; two isomers)[9] in THF yields the two phosphane complexes **6b** and **7b**, which can be distinguished by ^{31}P NMR spectroscopy (**6b**, δ 54.1 ppm, d, $^1J_{PH}$ = 429 Hz; **7b**, δ 65.4 ppm, dd, $^1J_{PH}$ = 439 Hz, $^2J_{PH}$ = 20 Hz). Pentane extraction allows one to isolate ((*tert*-butylamino)((trimethylsilyl)*tert*-butylamino)phosphane)tetracarbonyliron (**7b**), while **6b** disappears during workup. This may be ascribed to the loss of the Cp_2ZrCl fragment (hydrolysis of the zirconium–nitrogen bond) and, therefore, transformation of **6b** into **7b**. NMR data, mass spectrometry, and microanalysis support the proposed structure.[10] Addition of an excess of $Fe_2(CO)_9$ to a solution of the zirconaazaphosphirane **3a** gives rise to a similar phosphine complex, (((trimethylsilyl)amino)(bis(trimethylsilyl)amino)phosphane)tetracarbonyliron (**7a**)[10] (Scheme I).

Scheme II



Elemental sulfur and selenium also react very slowly with **3a**, leading to the ((trimethylsilyl)amino)(bis(trimethylsilyl)amino)phosphane sulfide (**8a**) and selenide (**8a′**), respectively.[11]

While reactions of species **3** with $Fe_2(CO)_9$, S_8, or Se proceed with ring opening, ring retention is observed when **3a** is reacted with trimethylsilyl trifluoromethanesulfonate or methyl trifluoromethanesulfonate in dichloromethane. The triflate derivative, namely bis(cyclopentadienyl)(trifluoromethanesulfonato)(trimethylsilyl)(bis(trimethylsilyl)amino)zirconaazaphosphirane (**9**), is obtained in nearly quantitative yield[10] (**9**: $\delta(^{31}P)$ = 40.9 ppm, $^1J_{PH}$ = 353 Hz) (Scheme II). Due to the oxophilicity of zirconium, a covalent Zr–O bond is expected. Indeed, the compound is soluble in nonpolar solvents and a band at 1377 cm^{-1} that can be assigned to covalently bound triflate[12] is detected in its infrared spectrum. Evaporation of dichloromethane followed by addition of a polar solvent such as acetonitrile leads to dissociation of the Zr–O bond and the formation of the ionic zirconium species **10**[10] ($\delta(^{31}P)$ = 28.9 ppm, $^1J_{PH}$ = 377 Hz; IR $\nu(SO_3)$ 1270 cm^{-1}, ionic triflate[12]). Removal of acetonitrile followed by addition of THF results in the recovery of the neutral species **9**. Conductometric measurements in acetonitrile definitely confirm the ionic character of **10**. The equivalent conductance of **10**, measured for a 0.01 M solution at 24 °C, is 97 mho cm^2 equiv^{-1}.

A facile anion exchange occurs when the bis(cyclopentadienyl)(trimethylsilyl)(bis(trimethylsilyl)amino)zirconaazaphosphirane cation **10** is reacted with $NaBPh_4$ in acetonitrile. The stable 18-electron complex **11** is obtained as a yellow powder.[10] Conductometric measurements in acetonitrile also demonstrate the ionic character of **11** (equivalent conductance of **11** 70 mho cm^2 equiv^{-1}). As expected in this case, no change is observed when **11** is dissolved in THF. **11** can be formed directly by reacting **3a** in acetonitrile solution with $NaBPh_4$. The large phosphorus–proton coupling constants detected in **9**–**11** are in agreement with ring retention and not with the acyclic form $[(Me_3Si)_2NP(H)N(SiMe_3)ZrCp_2CH_3CN][X]$ (X = CF_3SO_3, BPh_4).[3] The surprising stability of cations **10** and **11** can be rationalized in terms of charge delocalization along the P–N–Zr skeleton.

A study on the reactivity of these new cationic complexes

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(8) Karsch, H. H.; Denbelly, B.; Hofmann, J.; Pieper, U.; Müller, G. *J. Am. Chem. Soc.* **1988**, *110*, 3654.

(9) The cyclic complex **3b** was obtained as two isomers by reacting $Me_3SiN(tBu)P{=}NtBu$[16] with Cp_2ZrHCl [$\delta(^{31}P)$ = 3.4 ppm, d, $^1J_{PH}$ = 334 Hz (major); $\delta(^{31}P)$ −12.2 ppm, d, $^1J_{PH}$ = 337 Hz (minor)].

(10) Main spectroscopic data for **7a**: ^{31}P NMR (C_6D_6) δ 87.6 (d, $^1J_{PH}$ = 407 Hz); ^1H NMR (C_6D_6) δ 0.01 (s, 9 H, $NHSi(CH_3)_3$), 0.29 (s, 18 H, $N[Si(CH_3)_3]_2$), 7.7 (dd, $^1J_{PH}$ = 407 Hz, $^3J_{HH}$ = 8 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 2.5 (s) and 3.8 (s) ($Si(CH_3)_3$), 215.1 (d, $^2J_{CP}$ = 21.3 Hz, CO); IR (toluene) 2054 (m), 1971 (m), 1928 (s) (ν(CO)) cm^{-1}; mass spectrum *m/e* 448. Anal. Calcd for $C_{13}H_{29}FeN_2O_4PSi_3$: C, 34.82; H, 6.52; N, 6.25. Found: C, 34.76; H, 6.47; N, 6.19. Main spectroscopic data for **7b**: ^{31}P NMR (C_6D_6) δ 65.4 (dd, $^1J_{PH}$ = 435 Hz, $^2J_{PH}$ = 20 Hz); ^1H NMR (C_6D_6) δ 0.26 (s, 9 H, $Si(CH_3)_3$), 0.97 (s, 9 H, $C(CH_3)_3$), 1.16 (s, 9 H, $C(CH_3)_3$), 7.90 (dd, $^1J_{PH}$ = 435 Hz, $^3J_{HH}$ = 7 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 5.6 (d, $^3J_{CP}$ = 3.8 Hz, $Si(CH_3)_3$), 30.0 (d, $^3J_{CP}$ = 4.2 Hz, $C(CH_3)_3$), 33.1 (d, $^3J_{CP}$ = 4.7 Hz, $C(CH_3)_3$), 54.3 (d, $^2J_{CP}$ = 13.4 Hz, $C(CH_3)_3$), 58.4 (s, $C(CH_3)_3$), 215.2 (d, $^2J_{CP}$ = 20.8 Hz, CO); IR (pentane) 2045 (m), 1970 (s), 1925 (s) (ν(CO)) cm^{-1}; mass spectrum *m/e* 416. Anal. Calcd for $C_{15}H_{29}FeN_2O_4PSi$: C, 43.28; H, 7.02; N, 6.73. Found: C, 43.19; H, 7.11; N, 6.64. Main spectroscopic data for **9**: ^{31}P NMR (C_6D_6) δ 40.9 (d, $^1J_{PH}$ = 353 Hz); ^1H NMR (C_6D_6) δ 0.30 (s, 18 H, $N[Si(CH_3)_3]_2$), 0.32 (s, 9 H, $NSi(CH_3)_3$), 5.96 (d, J_{HP} = 2.75 Hz, 5 H, Cp), 6.11 (d, J_{HP} = 1.79 Hz, 5 H, Cp), 6.89 (d, $^1J_{HP}$ = 353 Hz, 1 H, P–H); ^{13}C NMR (C_6D_6) δ 2.7 (d, J_{CP} = 2.6 Hz) and 4.1 (br s, $NSi(CH_3)_3$), 110.5 (d, J_{CP} = 1.2 Hz, Cp), 111.4 (s, Cp), 120.2 (q, $^1J_{CF}$ = 319 Hz, CF_3SO_3); IR (KBr) 1377 ($\nu(SO_3)$) cm^{-1}. Anal. Calcd for $C_{20}H_{38}F_3N_2O_3PSSi_3Zr$: C, 36.95; H, 5.89; N, 4.31. Found: C, 36.86; H, 5.77; N, 4.18. Main spectroscopic data for **10**: ^{31}P NMR (CD_3CN) δ 28.9 (d, $^1J_{PH}$ = 377 Hz); ^1H NMR (CD_3CN) δ 0.28 (s, 9 H, $NSi(CH_3)_3$), 0.53 (s, 18 H, $N[Si(CH_3)_3]_2$), 2.09 (s, free CH_3CN; due to the CD_3CN–CH_3CN fast exchange, coordinated CH_3CN is not seen in CD_3CN solution), 6.16 (d, J_{HP} = 2.58 Hz, 5 H, Cp), 6.27 (d, J_{HP} = 1.73 Hz, 5 H, Cp), 7.18 (d, $^1J_{HP}$ = 377 Hz, 1 H, P–H); ^{13}C NMR (CD_3CN) δ 3.1 (d, J_{CP} = 2.6 Hz) and 4.3 (s, $NSi(CH_3)_3$), 110.6 and 111.5 (s, Cp), 120.2 (q, $^1J_{CF}$ = 319 Hz, CF_3SO_3); IR (CD_3CN) 1270 ($\nu(SO_3)$ ionic) cm^{-1}. Anal. Calcd for $C_{22}H_{41}F_3N_3O_3PSSi_3Zr$: C, 38.24; H, 5.98; N, 6.08. Found: C, 38.11; H, 5.91; N, 5.94. Main spectroscopic data for **11**: ^{31}P NMR (CH_3CN) δ 29.1 (d, $^1J_{PH}$ = 377 Hz); ^1H NMR (CD_3CN) δ 0.41 (s, 9 H, $NSi(CH_3)_3$), 0.66 (s, 18 H, $N[Si(CH_3)_3]_2$), 2.09 (s, free CH_3CN; coordinated CH_3CN in CD_2Cl_2 solution 1.60 (s, 3 H)), 6.19 (d, J_{HP} = 2.6 Hz, 5 H, Cp), 6.30 (d, J_{HP} = 1.8 Hz, 5 H, Cp), 7.23 (m, 12 H, *p*-, *m*-$(C_6H_5)_4B$), 7.29 (d, $^1J_{HP}$ = 377 Hz, 1 H, PH), 7.59 (m, 8 H, *o*-$(C_6H_5)_4B$); ^{13}C NMR (CD_3CN) δ 3.5 and 4.7 (s, $NSi(CH_3)_3$), 110.7 and 111.6 (s, Cp), 123.0 (s), 126.9 (q, J_{CB} = 2.7 Hz), 137 (s) and 165.1 (q, J_{BC} = 50 Hz, $(C_6H_5)_4B$); IR (CH_2Cl_2) 2302 and 2253 (ν(CN), free CH_3CN), 2281 (ν(CN), coordinated CH_3CN) cm^{-1}. Anal. Calcd for $C_{45}C_{61}BN_3PSi_3Zr$: C, 62.76; H, 7.14; N, 4.88. Found: C, 62.64; H, 7.10; N, 4.76.

(11) Niecke, E.; Ringel, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 486.

(12) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673 and references therein.

(13) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *39A*, 158.

(14) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. Crystals, an Advanced Crystallographic Program System; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1988.

(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(16) Scherer, O. J.; Kuhn, N. *Angew. Chem., Int. Ed. Engl.* **1974**, *86*, 899.

is underway.

Acknowledgment. Thanks are due to Dr. Jean-Claude Daran for the X-ray structure determination and for helpful discussions.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters, bond distances and angles, and least-squares planes (6 pages); a table of structure factors (9 pages). Ordering information is given on any current masthead page.

Phase-Transfer-Catalyzed Cleavage of Carbon–Hydrogen and Carbon–Phosphorus Bonds in PPh_3 by an Iridium Complex. Synthesis and Molecular Structure of $[Ir_2(C_5Me_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_4)]$

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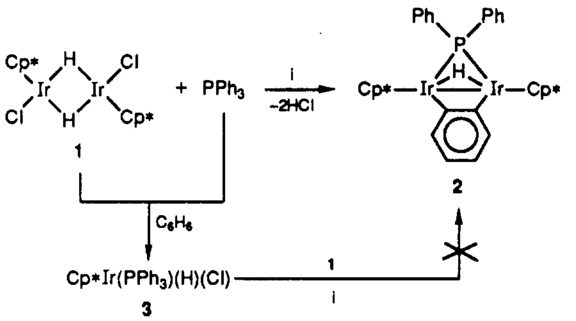
Received April 24, 1990

Summary: Reaction of $[(C_5Me_5IrCl)_2(\mu\text{-}H)_2]$ (**1**) with PPh_3 in benzene/60% aqueous $KOH/[PhCH_2NEt_3]^+Cl^-$ leads to the elimination of 2 equiv of HCl from **1**, oxidative addition of C–P and C–H bonds to iridium, and formation of the dinuclear complex $[Ir_2(C_5Me_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_4)]$ (**2**); the X-ray structure of **2** showed that it has bridging hydrido, diphenylphosphido, and *o*-phenylene ligands.

Phase-transfer catalysis (PTC) can be effectively used for the α-elimination of HCl from mononuclear chloro hydrido complexes of platinum,[1] iridium,[2,3] ruthenium,[3,4] and rhodium[3,4] and for the generation of reactive, coordinatively unsaturated complexes or their synthons. Here, we report the first and novel example of HCl elimination from a dinuclear chloro hydrido transition-metal complex under PTC conditions.

The reaction of $[\{(C_5Me_5)IrCl\}_2(\mu\text{-}H)_2]$ (1)[5] with PPh_3 in benzene/60% aqueous KOH, with $[PhCH_2NEt_3]^+Cl^-$ as the phase-transfer catalyst, resulted in the elimination of two molecules of HCl from 1 and formation of the new complex $[Ir_2(C_5Me_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_4)]$ (2; yield 50–60%, based on ^1H NMR spectroscopy) with bridging hydrido, diphenylphosphido, and *o*-phenylene ligands.[6] ^1H NMR spectroscopy[7] revealed that the reaction mixture contains another complex (3; ca. 30%), which is thought to arise from a known homogeneous reaction between 1 and PPh_3[5] (Scheme I).

Scheme I[a]



[a] Cp* = η^5-C_5Me_5. The letter i denotes PhH/60% aqueous $KOH/[PhCH_2NEt_3]^+Cl^-$.

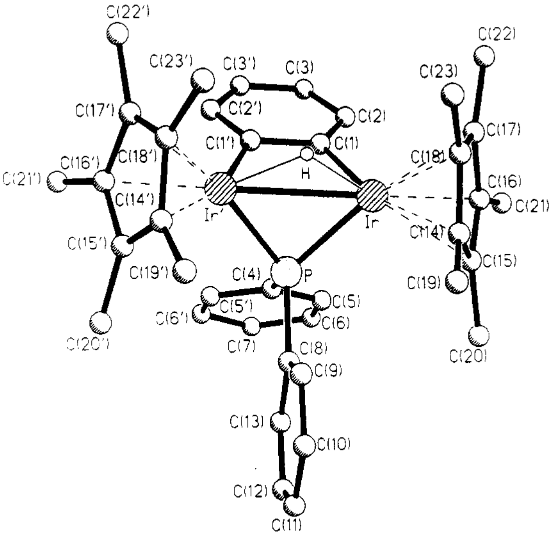


Figure 1. Molecular structure of 2. Selected bond lengths (Å) and bond angles (deg) are as follows: Ir–Ir', 2.8901 (4); Ir–P, 2.263 (2); Ir–C(1), 2.070 (7); Ir–H, 1.83 (8); C(1)–C(1'), 1.40 (1); P–C(4), 1.82 (1); P–C(8), 1.80 (1); ∠Ir–H–Ir', 105 (5); ∠Ir–P–Ir', 79.36 (8); ∠Ir'–Ir–C(1), 68.9 (2).

That 3 is a byproduct of the above reaction and not an intermediate in the formation of 2 was clearly established by noting that 1 and 3 were mixed under the same PTC conditions as above but 2 did not form in the absence of added PPh_3. Note that 3 does not undergo HCl elimination under these PTC conditions.

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(1) Grushin, V. V.; Akhrem, I. S.; Vol'pin, M. E. *Metalloorg. Khim.* **1988**, *1*, 474; *J. Organomet. Chem.* **1989**, *371*, 403.

(2) Grushin, V. V.; Bakhmutov, V. I.; Akhrem, I. S.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR. Ser. Khim.* **1988**, 494.

(3) Grushin, V. V.; Vymenits, A. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *382*, 185.

(4) Grushin, V. V.; Vymenits, A. B.; Vol'pin, M. E. *Metalloorg. Khim.* **1990**, *3*, 702.

(5) Gill, D. S.; Maitlis, P. M. *J. Organomet. Chem.* **1975**, *87*, 359.

(6) In a typical experiment, a mixture of 1[5] (299 mg; 0.41 mmol), PPh_3 (190 mg; 0.74 mmol), $[PhCH_2NEt_3]^+Cl^-$ (90 mg; 0.4 mmol), benzene (5 mL), and 60% aqueous KOH (5 mL) was vigorously stirred under argon at 20 °C for 8 h. The organic layer was separated and evaporated to dryness, and the residue was washed with hot MeOH (4 × 6 mL) to give reddish orange crystals of **2**: yield 131 mg (35%); mp >250 °C dec. Anal. Calcd for $C_{38}H_{45}Ir_2P$: C, 49.8; H, 5.0. Found: C, 50.1; H, 5.1. ^1H NMR for **2** (200 MHz, cyclohexane-d_{12}, 25 °C): δ −17.7 (d, 1 H, Ir–H–Ir, J(P–H) = 18 Hz), 1.9 (d, 30 H, CH_3, J(P–H) = 1.7 Hz), 6.0 (m, 2 H, 3,6-H), 6.2 (m, 2 H, 4,5-H), 6.8–7.3 (m, 10 H, C_6H_5).

(7) ^1H NMR for **3** (200 MHz, benzene-d_6, 25 °C): δ −13.2 (d, 1 H, Ir–H, J(P–H) = 36.5 Hz), 1.5 (dd, 15 H, CH_3, J(P–H) = 1.9 Hz, J(H–H) = 0.8 Hz), 7.5 (m, 15 H, C_6H_5). Compare this to the spectrum published in: Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. A* **1970**, 2875.