1692 *Organometallics* **2000,** *19,* 1692−1694

Unsymmetrically Substituted Iridium(III)−Carbene Complexes by a CH-Activation Process†

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Received October 8, 1999

The synthesis of the metalhydride Cp*(L′)IrH$^+$OTf$^-$ (L′ = 1-(2-cyclohexenyl)-3-cyclohexylimidazolin-2-ylidene, OTf = OSO_2CF_3) is achieved by a cyclohexane to cyclohexene transformation at the *N*-heterocyclic carbene ligand based on a CH-activation/β-hydrogen migration process at the Ir(III) center under mild conditions. The synthetic route to Cp*(L′)IrH$^+$OTf$^-$ and NMR spectroscopic and X-ray structural data are presented.

Introduction

Transition metal complexes with *N*-heterocyclic carbene ligands have recently proved to be very efficient catalysts.[1−3] The catalytic activity is influenced by the substituents at the carbene ligand.[3] In general the substituents are first introduced into the *N*-heterocyclic carbene, and the latter is subsequently coordinated to a metal center. Another possibility would be the coordination of the *N*-heterocyclic carbene to the metal center and the subsequent activation and functionalization of the substituents.

The selective activation and functionalization of CH bonds has attracted increased attention in recent years.[4] Bergman et al.[5a−c] have reported Cp*Ir^{III}(P(CH$_3$)$_3$)(CH$_3$)$^+$X$^-$ complexes that activate CH bonds under very mild conditions. Lappert et al. have reported the activation of an aromatic CH bond at an *N*-heterocyclic carbene, forming an orthometalated Ir(III) complex.[5d] Chaudret et al.[6a] and Vrieze et al.,[6b] respectively, have shown that a dehydrogenation of cyclohexyl phosphine ligands occurs at ruthenium(II) and iridium(I) centers, respectively.

Herein, we report the synthesis of a new type of Ir(III)−carbene complexes, Cp*(L′)IrH$^+$OTf$^-$ (L′ = 1-(2-cyclohexenyl)-3-cyclohexylimidazolin-2-ylidene, OTf = OSO_2CF_3), based on the activation and subsequent functionalization of one cyclohexyl substituent at the *N*-heterocyclic carbene by a CH-activation/β-hydrogen migration process at the iridium(III) center.

Results and Discussion

Treatment of [Cp*IrCl$_2$]$_2$ (**1**)[7] (Cp* = [η^5-C$_5$(CH$_3$)$_5$]) with 1 equiv of 1,3-dicyclohexylimidazolin-2-ylidene[2] yields the new carbene complex **2** as a yellow, air-stable solid (Figure 1). **2** contains an *N*-heterocyclic carbene and a cyclopentadienyl ligand ($\delta(C_c)$ = 153.5 ppm, $\delta(C_{Cp*})$ = 88.6 ppm, and $\delta(CH_{3Cp*})$ = 8.9 ppm, respectively). Further reaction of **2** with 2 equiv of CH$_3$MgCl yields the colorless dimethyl complex **3** ($\delta(CH_3) = -0.11$ ppm, $\delta(CH_3) = -20.9$ ppm). To replace one methyl group by triflate, **3** was treated with 1 equiv of trifluoromethylsulfonic acid. Reaction occurred with immediate gas evolution (CH$_4$) and formation of a metal hydride **4** ($\delta(IrH) = -16.30$ ppm) as pale yellow crystals. The single-crystal X-ray analysis (Figure 2, Table 1) showed the cyclopentadienyl and the carbene ligand being attached to the iridium center with significant bond lengths of 1.895 Å (C_{g1}−Ir) and 2.019(4) Å (Ir−C$_1$). Attached to the carbene moiety, one of the six-membered rings remains unchanged, whereas the other one shows a short C$_5$−C$_6$ distance, 1.400(8) Å, typical of π-coordinated double bonds.[5a,8] The evidence of an alkene coordinated to the iridium is supported by the similar distances of the C$_5$ and C$_6$ carbons to the iridium: 2.145-

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[†] Heterocyclic Carbenes 21. Part 20: Herrmann, W. A.; Schwarz, J.; Gardines, M. G.; Spiegler, M. *J. Organomet. Chem.* **1999**, *575*, 80−86.

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(9) The X-ray structure indicates the presence of a hydride because the sum of the bond angles around the metal center (346°) indicates a distorted tetrahedric coordination rather than a trigonal planar coordination.

10.1021/om990804r CCC: $19.00

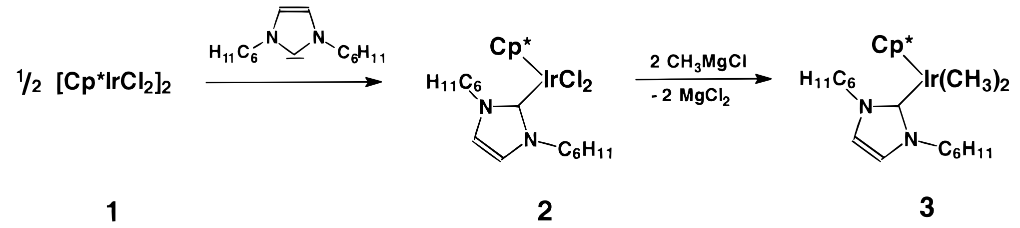

Figure 1. Cp* = [η^5-$C_5(CH_3)_5$].

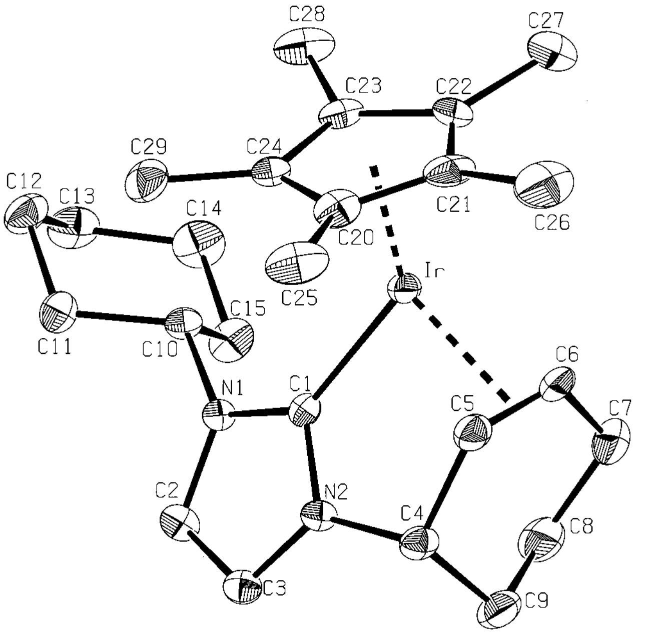

Figure 2. PLATON plot of the cation of **4**. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ir−C_{g1} 1.895, Ir−C_{g2} 2.044, Ir−C_5 2.145(5), Ir−C_6 2.177(5), Ir−C_1 2.019(4), C_5−C_6 1.400(8); C_{g1}−Ir−C_{g2} 127.09, C_{g1}−Ir−C_1 131.30, C_{g2}−Ir−C_1 87.75, C_{g1}−Ir−C_5 123.23, C_1−Ir−C_5 77.83(17), C_5−Ir−C_6 37.8(2).

(5) and 2.177(5) Å, respectively. IR and NMR data prove the presence of a hydride at the metal center, fully in accord with the overall geometry of the complex.[9]

Mechanistically, it is likely that treatment of **3** with 1 equiv of trifluoromethylsulfonic acid results in methane elimination, giving the expected triflate complex, which then, however, undergoes further reaction (Figure 3).

It is reasonable to assume that the resulting triflate complex is involved in an equilibrium in solution, affording the dissociation of the triflate ligand to build up a 16e species **A**, which might be stabilized by a solvent molecule. In a CH-activation process of one of the CH bonds of a cyclohexyl ring a second equivalent of methane is eliminated to form **B**. The latter undergoes β-hydrogen migration to yield **4**. This mechanism is in agreement with a previous suggestion of Bergman et al.[8c] The cyclometalation/β-hydrogen migration results in the formation of chiral centers at the iridium and at the C_4 carbon (Figure 2). Theoretically four isomers could thus occur, constituting two pairs of enantiomers. According to the ^{1}H NMR, which shows only one hydride signal, the X-ray structural data, the geometry, and the centrosymmetric space group, we assume that only the two enantiomers Ir_SC_R and Ir_RC_S are formed.[10] This is in accordance with the suggested mechanism: in the cyclometalation step the chiral center at the C_4 carbon is fixed and the subsequent β-hydrogen migration occurs always with syn-geometry so that only the experimentally found enantiomers can be formed.

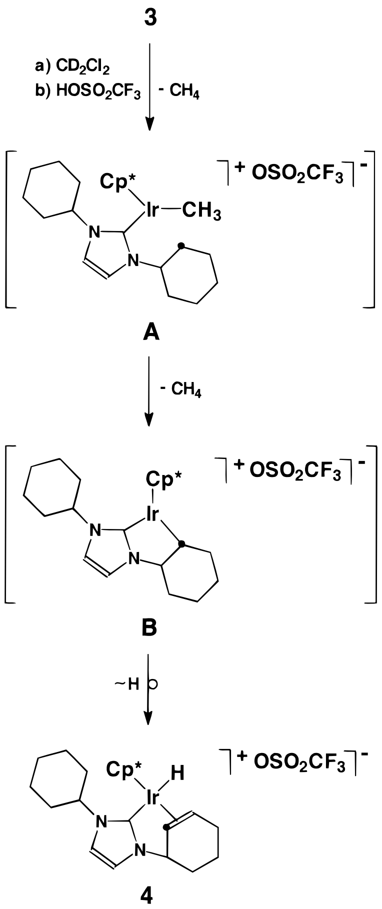

Figure 3. Cp* = [η^5-$C_5(CH_3)_5$]. Solvent effects are disregarded.

The reported CH-activation/β-hydrogen migration process leads to the selective activation of one cyclohexyl ring at the *N*-heterocyclic carbene ligand. The resulting double bond promises an entry into further functionalization.

Experimental Section

General Comments. All manipulations were carried out under dry nitrogen by using standard Schlenk techniques. The solvents were dried by standard procedures. 1,3-Dicyclohexylimidazolin-2-ylidene (L)[2] was prepared according to the literature procedure, as was $[Cp^*IrCl_2]_2$ (**1**).[7]

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[10] For R/S convention, see: Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1−36.

Table 1. Crystal Data and Details of the Structure Determination for Compound 4

formula	$C_{26}H_{38}F_3N_2O_3SIr$
fw	707.87
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a [Å]	10.3863(7)
b [Å]	15.6162(6)
c [Å]	17.2212(11)
β [deg]	103.429(7)
V [Å^3]	2716.8(3)
Z	4
ρ_{calcd} [g/cm^3]	1.731
μ [1/mm]	5.0
F_{000}	1408
cryst size [mm]	$0.102 \times 0.381 \times 0.813$
T [K]	173
λ [Å]	0.71073
monochromator	graphite
hkl range	-12: 12; -18: 18; -20: 20
$\theta_{min/max}$	2.1/25.6
total no. of data	37067
no. of unique data	5046
no. of obsd data [$I > 2\sigma(I)$]	4272
R_{int}	0.0803
R1[a] (all data)	0.0342
wR2[b] (all data)	0.0870
goodness of fit[c]	0.97
$\Delta\rho_{min/max}$ [e/Å^3]	$-2.66/1.56$

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $gof = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

Preparation of Cp*(L)IrCl$_2$ (2). A stirred suspension of 698 mg (0.88 mmol) of **1** in 35 mL of THF was cooled to −78 °C and treated with a solution of 465 mg (2.00 mmol) of 1,3-dicyclohexylimidazolin-2-ylidene in 12 mL of THF. The mixture was allowed to warm to 0 °C, stirred for 1 h, and then stirred at room temperature for 12 h. The solvent was removed in vacuo. The residue was washed with *n*-hexane and chromatographed over a column of silica gel with methylene chloride/tetrahydrofuran (tetrahydrofuran 10%). The product-containing fractions were combined and evaporated. Yield: 1.0 g (90%). Orange crystals were obtained by slow concentration of a solution of **2** in acetone. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C; ppm): $\delta = 7.04$ (s, 2 H, CH_c), 4.77 (m, 2 H, CH_{cy}), 2.50−1.20 (m, 20 H, CH_{2cy}), 1.57 (s, 15 H, CH_{3Cp*}). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 25 °C; ppm): $\delta = 153.5$ (C_c), 119.0 (CH_c), 88.6 (C_{Cp*}), 58.4 (CH_{cy}), 35.9, 35.2, 25.7, 25.4, 25.3 (CH_2), 8.9 (CH_{3Cp*}). MS (CI; *m*/*z*): 631 [MH$^+$] (correct isotopic pattern), 596 [MH$^+$ − Cl], 560 [M$^+$ − 2Cl], 232 [carb$^+$]. Anal. Calcd for $C_{25}H_{39}Cl_2N_2Ir\cdot(CH_3)_2CO$ (688.803): C, 48.82; H, 6.58; N, 4.07. Found: C, 48.65; H, 6.50; N, 4.19.

Preparation of Cp*(L)Ir(CH$_3$)$_2$ (3). A 580 mg (0.92 mmol) sample of **2** was suspended in 30 mL of THF and cooled to −78 °C. A 6.1 mL portion of a 0.3 M solution of the Grignard reagent was added slowly. The mixture was allowed to warm to room temperature and stirred for 3 h. After removal of the solvent in vacuo the residue was extracted twice with 30 mL of *n*-hexane. After evaporation to dryness under vacuum the product was obtained as a foam. Yield: 415 mg (77%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C; ppm): $\delta = 6.83$ (s, 2 H, CH_c), 4.44 (m, 2 H, CH_{cy}), 2.20−1.00 (m, 20 H, CH_{2cy}), 1.64 (s, 15 H, CH_{3Cp*}), −0.11 (s, 6 H, $IrCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 25 °C; ppm): $\delta = 163.3$ (C_c), 117.1 (CH_c), 87.4 (C_{Cp*}), 58.3 (CH_{cy}), 36.1, 35.9, 26.5, 26.3, 26.0 (CH_2), 8.9 (CH_{3Cp*}), −20.9 ($IrCH_3$). MS (CI; *m*/*z*): 591 [MH$^+$] (correct isotopic pattern), 575 [M$^+$ − CH$_3$], 560 [M$^+$ − 2CH$_3$]. Anal. Calcd for $C_{27}H_{45}N_2Ir$ (589.887): C, 54.98; H, 7.69; N, 4.75. Found: C, 54.95; H, 7.75; N, 4.63.

Preparation of Cp*(L′)IrH$^+$OTf$^-$ (4). A 200 mg (0.34 mmol) sample of **3** was dissolved in 4 mL of CD_2Cl_2. The solution was cooled to −78 °C, and 30 μL (0.34 mmol) of trifluoromethanesulfonic acid was added. After stirring for 10 min the cold bath was removed and the mixture was stirred for 3 h at room temperature. The solvent was evaporated. Pale yellow crystals were obtained by crystallization from methylene chloride/*n*-pentane. Yield: 170 mg (71%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C; ppm): $\delta = 7.01$ (d, $^3J(H,H) = 2.4$ Hz, 1 H, CH_c), 6.93 (d, $^3J(H,H) = 2.4$ Hz, 1 H, CH_c), 4.86, 4.37, 3.80, 3.61 (m, 4 H, CH_{cy} and CH_{olef}), 3.01−1.00 (m, 16 H, CH_2), 1.94 (s, 15 H, CH_{3Cp*}), −16.30 (s, 1H, IrH). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 25 °C; ppm): δ = CF_3 signal was not detectable, 145.4 (C_c), 120.0, 119.5 (CH_c), 99.0 (C_{Cp*}), 59.7, 55.9, 53.0, 52.9 (CH_{cy} and CH_{olef}), 34.1, 33.1, 32.7, 30.1, 26.0, 25.8, 25.3, 14.4 (CH_{2cy}), 9.6 (CH_{3Cp*}). IR (KBr): $\tilde{\nu} = 2117.0$ cm^{-1} (Ir−H). MS (FAB; *m*/*z*): 560 [cation of **4** + H] (correct isotopic pattern). Anal. Calcd for $C_{26}H_{38}F_3N_2O_3SIr$ (707.872): C, 44.12; H, 5.41; N, 3.96; F, 8.05. Found: C, 44.75; H, 5.47; N, 3.83; F, 7.59.

X-ray Structure Determination. (a) Crystal data and X-ray crystallography for $C_{26}H_{38}F_3N_2O_3SIr$, **4**: $M = 707.87$, monoclinic, $P2_1/n$, $a = 10.3863(7)$ Å, $b = 15.6162(6)$ Å, $c = 17.2212(11)$ Å, $\beta = 103.429(7)°$, $V = 2716.9(3)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.731$ gcm^{-3}, $F_{000} = 1408$, $\mu = 5.0$ mm^{-1}. Suitable crystals were obtained by slow diffusion of *n*-pentane into a solution of **4** in methylene chloride. Preliminary examination and data collection were carried out on an imaging plate diffraction system (STOE), a rotating anode (NONIUS FR591), and graphite-monochromated Mo Kα radiation. Data collection was performed at 173 K within the θ-range of $2.1° < \theta < 25.6°$. A total number of 37 067 reflections were collected and scaled. After merging ($R_{int} = 0.0803$), a sum of 5046 independent reflections remained and were used for all calculations. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the program DIFABS. The structure was solved by a combination of direct methods and difference Fourier syntheses. All "heavy atoms" of the asymmetric unit were refined anisotropically. All hydrogen atoms were calculated. The hydride atom could not be located. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the *SHELXL-93* weighting scheme and stopped at R1 = 0.0342, wR2 = 0.0870, GOF = 0.97, and shift/err < 0.001. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for X-ray Crystallograpy*. All calculations were performed on a Linux PC with the *STRUX-V* system, including the programs *PLATON-98*, *PLUTON-98*, *SIR-92*, and *SHELXL-93*. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-140424 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax (+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk). (b) c_{g1}: centroid of the cyclopentadienyl ring. (c) c_{g2}: centroid of the double bond.

Acknowledgment. This work received generous support from the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie, the Deutsche Forschungsgemeinschaft, and the Degussa-Hüls AG (loans of iridium(III) chloride).

Supporting Information Available: Complete tables of crystal data and refinement details, atomic positional and thermal parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990804R