Isolation, Characterization, and Interconversions of $(Et_3P)_2Ir(C_2H_4)_nCl$ ($n = 1, 2$)

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*Summary: The syntheses, characterization, and interconversions of $(Et_3P)_2Ir(C_2H_4)_2Cl$ (**1**) and $(Et_3P)_2Ir(C_2H_4)(Cl)$ (**2**) as well as the X-ray crystal structure of **1** are reported. In solution complex **1** has a stereochemically rigid trigonal-bipyramidal structure with nonrotating ethylene ligands. Formation of complex **1** from complex **2** and ethylene is thermodynamically favorable; $\Delta G_{298} = -2.12 \pm 0.03$ kcal/mol.*

Introduction

The electron-rich iridium ethylene complexes $(Et_3P)_2Ir(C_2H_4)_2(Cl)$ (**1**) and $(Et_3P)_2Ir(C_2H_4)(Cl)$ (**2**) are capable of N-H activation of ammonia and aniline,[1] including hydroamination of norbornene. Complex **2** was also used as a precursor for the synthesis of metallosilanols[2] and other silane adducts[3] by Si−H oxidative addition. However, the synthesis and characterization of complexes **1** and **2** have not been described in full. In the present note we report on (i) the preparation and NMR spectroscopic properties of both of these complexes, (ii) their interconversions in solution, and (iii) the X-ray structure of **1**.

Results and Discussion

The room-temperature reaction of $[(C_8H_{14})_2IrCl]_2$ with 4 equiv of PEt_3 in pentane with subsequent pressurizing of the resulting solution with ethylene leads to formation of a gray precipitate. According to elemental analysis data, the compound obtained by this procedure has a stoichiometry of $(Et_3P)_2Ir(C_2H_4)_2(Cl)$. However, the NMR spectra of benzene or THF solutions of the gray compound show the presence of more than one species. The $^{31}P\{^1H\}$ NMR spectrum contains as major signals two mutually coupled doublets at δ −34.0 and −22.6 ppm ($J = 10.8$ Hz) and a singlet at δ 8.4 ppm in an approximately 8:1 ratio. Multiple extraction of this gray solid with warm pentane in an open vessel under an N_2 atmosphere dissolves it almost without loss. Evaporation of the solvent of the resulting orange solution leaves orange-red crystals. The $^{31}P\{^1H\}$ NMR spectrum of a benzene solution of these crystals reveals the presence of only one singlet at δ 8.4 ppm, thus indicating that all the species that contain triethylphosphine can be converted into a single complex having equivalent PEt_3 groups. ^1H and $^{13}C\{^1H\}$ NMR spectra (see below) together with elemental analysis data allowed unequivocal identification of this compound as *trans*-$(Et_3P)_2Ir(C_2H_4)(Cl)$ (**2**).

The coordinated ethylene gives rise in the ^1H NMR spectrum of **2** to a triplet at δ 1.74 ppm with the coupling constant $^3J(H,P) = 4.4$ Hz. The triplet transforms to a singlet upon decoupling of phosphorus. We note that reported analogs of **2** that have instead of triethylphosphine the ligands PPh_3,[4] P^iPr_3,[5] and $P^iPr_2(CH_2CH_2OMe)$[6] likewise exhibit in ^1H NMR spectra triplets with $^3J(H,P) \approx 4$ Hz for the CH_2 protons of the coordinated ethylene ligands. The $^{13}C\{^1H\}$ NMR spectrum of **2** contains, in addition to the signals of triethylphosphine carbon atoms, a triplet at δ 17.55 ppm with a small $^2J(C,P_{cis}) = 1.8$ Hz due to two equivalent ethylene carbons. These spectral features are fully consistent with the square-planar geometry of the complex having the ethylene molecule oriented perpendicular to the plane defined by Ir, Cl, and P atoms. Indeed, the PPh_3 analog of **2** was shown by X-ray studies to have such a structure.[7]

Washing the gray solid with cold pentane followed by recrystallizing from toluene (−20 °C) allows us to isolate an analytically pure crystalline compound, which gives rise to the two-doublet pattern in the ^{31}P NMR spectrum. Its ^1H and $^{13}C\{^1H\}$ NMR spectra, measured in the absence of other components of the mixture, proved that it is the pentacoordinate bis(ethylene) bis(phosphine) complex **1** rather than the initially proposed[1c] mono(ethylene) square-planar cis isomer of **2**.

The eight ethylene hydrogens give rise in the ^1H NMR spectrum of **1** to four multiplets at δ 2.40, 2.50, 2.73, and 3.11 ppm, each of which is integrated as two protons. The multiplets are mutually coupled, which is clearly seen in the $^1H-^1H$ COSY spectrum. They also exhibit $^3J_{H,P}$ couplings that are suppressed in the $^1H\{^{31}P\}$ NMR spectrum. Resonances of the four ethylene carbons are split by two different phosphorus nuclei and appear in the $^{13}C\{^1H\}$ NMR spectrum as two doublets of doublets with characteristic coupling constants at δ 28.41 and 28.74 ppm. The data of the $^{13}C-^1H$ correlation together with that of the $^1H-^1H$ COSY spectrum allow us to completely assign the proton and the carbon resonances of the C_2H_4 ligands, as shown in Figure 1.

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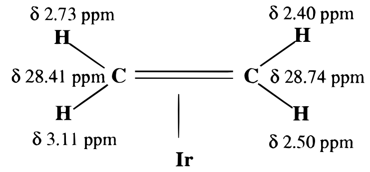

Figure 1. Assignment of the proton and carbon resonances of the C_2H_4 ligands in **1**.

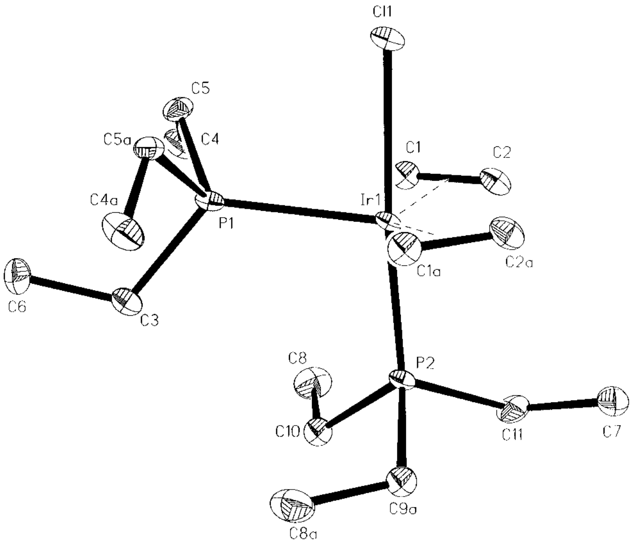

Figure 2. Perspective view of a molecule of **1**.

These data clearly indicate that in solution the coordinated ethylene ligands of **1** are equivalent and nonrotating, the complex itself being stereochemically rigid. Although not very common, such stereochemical rigidity was observed for similar electron-rich bis(ethylene) complexes of Os(0) and Ir(I) such as $(Me_3P)_2Os(C_2H_4)_2(CO)$[8] and $[(Me_2PhP)_3Ir(C_2H_4)_2][BF_4]$[9] and also supported by calculations.[9b]

Final verification of the structure of **1** came from an X-ray crystallographic study (Figure 2, Tables 1−3). Complex **1** adopts a distorted-trigonal-bipyramidal structure with (as predicted by theory[10]) two ethylenes in the equatorial plane. The third place in the plane is occupied by one of the phosphines, while the remaining phosphine and chloride ligands are located in the axial positions. Several structural features are immediately evident from examining Figure 2 and Tables 2 and 3. Distortions of the geometry of **1** from a trigonal bipyramid are not very significant. The angle P(2)−Ir(1)−Cl(1) is only slightly less than 180°; the two ethylenes, Ir(1), and P(1) do not deviate much from the equatorial plane. Bond angles involving the centers of C(1)−C(2) (A) and C(1a)−C(2a) (B) are P(1)−Ir(1)−A = 113.8° and A−Ir(1)−B = 129.1°. The bond $Ir(1)-P(2)_{\text{trans to Cl}}$ (2.258(3) Å) is significantly (by more than 0.13 Å) shorter than Ir(1)−P(1) (2.394(3) Å). The Ir(1)−Cl(2) distance of 2.451(3) Å is quite normal. Despite a slight disorder which is involved in this structure, we believe that the following qualitative observations can nevertheless be made. The average *CPC* angle around P(1) equals 102.4° (the smallest one is 101.9(5)°), while that around P(2) is 99.0° (the smallest one is 97.4(8)°). Although the value of the *CPC* angle in free PEt_3 to our knowledge was not reported, it is very probably not less than the average value for $PEtMe_2$, which equals 100.2°.[11] Assuming that the structure of **1** in solution is similar to that in the solid state, we can conclude that the *CPC* angle of the axial triethylphosphine ligand not only **did not open up** on coordination, but rather it **contracted**. This may explain the relatively unusual high-field chemical shift value (δ −34.0 ppm) observed for this phosphorus atom in the ^{31}P NMR spectrum of **1**. The carbon−carbon bond lengths in the symmetry-related coordinated ethylenes in **1** have a value of 1.412(12) Å and are quite normal.[12] In accord with the equivalence of the ethylene ligands, in low-temperature ^1H and ^{13}C NMR spectra on cooling to −50 °C only four proton and two carbon signals are observed.

Table 1. Crystallographic Data for Complex 1

formula	$C_{16}H_{38}P_2ClIr$
mol wt	520.05
cryst syst	monoclinic
space group	$P2_1/m$ (No. 11)
a, Å	8.339(2)
b, Å	12.204(2)
c, Å	10.173(2)
β, deg	103.526(3)
V, Å^3	1006.6(4)
Z	2
d_{calcd}, g/cm^3	1.716
μ, mm^{-1}	6.916
diffractometer	Rigaku AFC5R, four circle
radiation (wavelength, Å)	Mo Kα (λ = 0.710 73)
monochromator	graphite
temp, K	110
mode	ω
$\theta_{\max}$, deg	27.5
scan speed, deg/min	8
scan width, deg	1.2
collecn range	$-10 \le h \le 10, -1 \le k \le 15, 0 \le l \le 13$
no. of rflns	
collected	5191
indep	2414
R_{int}	0.0712

Table 2. Selected Interatomic Bond Lengths (Å) for 1

Ir(1)−C(1)	2.178(9)	P(1)−C(5)	1.834(9)
Ir(1)−C(2)	2.140(9)	P(1)−C(3)	1.844(12)
Ir(1)−P(1)	2.394(3)	P(2)−C(9a)	1.82(2)
Ir(1)−P(2)	2.258(3)	P(2)−C(10)	1.85(2)
Ir(1)−Cl(1)	2.451(3)	P(2)−C(11)	1.88(2)
C(1)−C(2)	1.412(12)		

Table 3. Selected Bond Angles (deg) for 1

C(1)−Ir(1)−C(2)	38.2(3)	C(5)−P(1)−C(5a)	101.9(5)
C(1)−Ir(1)−C(1a)	165.0(4)	C(5)−P(1)−C(3)	102.7(4)
C(2)−Ir(1)−C(2a)	91.0(5)	C(9a)−P(2)−C(10)	98.5(8)
P(1)−Ir(1)−Cl(1)	82.87(10)	C(9a)−P(2)−C(11)	101.1(8)
P(1)−Ir(1)−P(2)	101.92(10)	C(10)−P(2)−C(11)	97.4(8)
P(2)−Ir(1)−Cl(1)	175.21(10)		

Complexes **1** and **2** are interconvertible. When a 0.089 M benzene solution of **2** is pressurized in a high-pressure NMR tube with 50 psi of ethylene at room temperature, **1** is quantitatively formed over a period of 5 min. When the ethylene atmosphere is displaced with argon, complex **2** starts to accumulate slowly until the equilibrium $\mathbf{2} + C_2H_4 \rightleftharpoons \mathbf{1}$ is reached. Concentrations of **1**, **2**, and C_2H_4, determined from the carefully

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integrated ^{1}H and ^{31}P NMR spectra of the mixture, stabilized after 2 days and remained unchanged over an additional 7 days. The equilibrium constant, estimated from the NMR data, is $K_{eq}(298\ \mathrm{K}) = [\mathbf{1}]/([\mathbf{2}][\mathrm{C_2H_4}]) = 36 \pm 2$, corresponding to $\Delta G_{298} = -2.12 \pm 0.03$ kcal/mol. The fact that at room temperature formation of the bis(ethylene) complex **1** from complex **2** and ethylene is thermodynamically favorable is in sharp contrast with the situation observed for analogous $\mathrm{PPh_3}$ complexes, for which the bis(ethylene) adduct was reported to be unstable to the loss of one ethylene ligand at temperatures higher than −50 °C.[4] The observed stability of **1** is in full accord with the strong electron-donating character of the $\mathrm{PEt_3}$ ligands that causes an increase of iridium-to-ethylene back-bonding and a corresponding strengthening of the Ir-$\mathrm{C_2H_4}$ bond.

Experimental Section

General Comments. The compounds described herein are air-sensitive and were handled in a nitrogen-filled drybox or using standard Schlenk techniques. The solvents used were prepurified and dried by established procedures. $[\mathrm{Ir(C_8H_{14})_2Cl}]_2$ was synthesized as described in the literature.[13] NMR spectra were measured with a Bruker AMX 400 spectrometer and were referenced as follows: ^{1}H (400 MHz), to the residual $\mathrm{C_6D_5H}$ at δ 7.15 ppm; ^{13}C (100 MHz), to the signal of $\mathrm{C_6D_6}$ at δ 128.00 ppm; ^{31}P (162 MHz), to the external 85% $\mathrm{H_3PO_4}$ in $\mathrm{D_2O}$ at δ 0.0 ppm. Elemental analyses were performed at the Microanalysis Laboratory of The Hebrew University of Jerusalem.

Preparation of *cis*-$\mathbf{(Et_3P)_2Ir(C_2H_4)_2(Cl)}$ (1). To a suspension of 400 mg (0.446 mmol) of $[\mathrm{Ir(C_8H_{14})_2Cl}]_2$ in 8 mL of pentane was added dropwise with stirring a solution of 215 mg (1.822 mmol) of $\mathrm{PEt_3}$ in 2.5 mL of pentane. The red solution formed was transferred to a Fischer−Porter flask, where it was pressurized with $\mathrm{C_2H_4}$ to 60 psi upon stirring. The procedure was repeated four times over 1 h, each time restoring the pressure after a small drop. When the mixture was stirred overnight, a fine gray precipitate was formed. The solvent was decanted and the precipitate was washed with 3 mL of pentane and dried under vacuum to yield 310 mg (~67%) of crude **1** as a gray powder. An analytically pure sample, for which spectral data are presented below, was obtained by recrystallization of the crude product from a minimum amount of toluene at −20 °C. Anal. Calcd for $\mathrm{C_{16}H_{38}ClIrP_2}$: C, 36.95; H, 7.36. Found: C, 36.70; H, 7.21. ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): δ −34.0 (d, ^{2}J(P,P) = 10.8 Hz, 1P), −22.6 (d, ^{2}J(P,P) = 10.8 Hz, 1P). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.53 (dt, ^{3}J(H,P) = 14.3 Hz, ^{3}J(H,H) = 7.6 Hz, 9H; $\mathrm{PCH_2C}H_3$), 0.90 (dq, ^{2}J(H,P) = 9.0 Hz, ^{3}J(H,H) = 7.7 Hz, 6H; $\mathrm{P{-}C}H_2\mathrm{CH_3}$), 0.98 (dt, ^{3}J(H,P) = 13.8 Hz, ^{3}J(H,H) = 7.6 Hz, 9H; $\mathrm{PCH_2C}H_3$), 1.97 (app quin, J = 7.6 Hz, 6H; $\mathrm{P{-}C}H_2\mathrm{CH_3}$), 2.40, 2.50, 2.73, 3.11 (multiplets, 2H each; $\mathrm{C_2}H_4$). ^{1}H{^{31}P} NMR ($\mathrm{C_6D_6}$): δ 0.52 (t, ^{3}J(H,H) = 7.6 Hz, 9H; $\mathrm{PCH_2C}H_3$), 0.89 (q, ^{3}J(H,H) = 7.7 Hz, 6H; $\mathrm{P{-}C}H_2\mathrm{CH_3}$), 0.97 (t, ^{3}J(H,H) = 7.6 Hz, 9H; $\mathrm{PCH_2C}H_3$), 1.97(q, ^{3}J(H,H) = 7.6 Hz, 6H; $\mathrm{P{-}C}H_2\mathrm{CH_3}$), 2.39 (dd, J_1 = 8.4 Hz, J_2 = 10.5 Hz, 2H; $\mathrm{C_2}H_4$), 2.50 (app t, J = 9.8 Hz, 2H; $\mathrm{C_2}H_4$), 2.73 (m, 2H; $\mathrm{C_2}H_4$), 3.12 (app t, J = 9.9 Hz, 2H; $\mathrm{C_2}H_4$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 8.32 (d, ^{2}J(C,P) = 4.6 Hz, positive in DEPT; $\mathrm{PCH_2}C\mathrm{H_3}$), 8.49 (d, ^{2}J(C,P) = 3.5 Hz, positive in DEPT; $\mathrm{PCH_2}C\mathrm{H_3}$), 16.30 (dd, ^{1}J(C,P) = 35.1 Hz, ^{3}J(C,P) = 3.1 Hz, negative in DEPT; $\mathrm{P}C\mathrm{H_2CH_3}$), 18.73 (d, ^{1}J(C,P) = 23.8 Hz, negative in DEPT; $\mathrm{P}C\mathrm{H_2CH_3}$), 28.41 (dd, $^{2}J(\mathrm{C,P_{eq}})$ = 15.8 Hz, $^{2}J(\mathrm{C,P_{ax}})$ = 1.3 Hz, negative in DEPT; $C_2\mathrm{H_4}$), 28.74 (dd, $^{2}J(\mathrm{C,P_{eq}})$ = 7.7 Hz, $^{2}J(\mathrm{C,P_{ax}})$ = 1.4 Hz, negative in DEPT; $C_2\mathrm{H_4}$).

Preparation of *trans*-$\mathbf{(Et_3P)_2Ir(C_2H_4)(Cl)}$ (2). A 130 mg (0.25 mmol) amount of crude (nonrecrystallized) **1** was repeatedly extracted in an open vessel under an $\mathrm{N_2}$ atmosphere with 2 mL portions of warm dry pentane upon rapid stirring. The orange extracts after filtration were combined (about 30 mL totally) and evacuated to dryness to yield 110 mg (~89%) of pure **2** in a form of red-orange plates. Anal. Calcd for $\mathrm{C_{14}H_{34}ClIrP_2}$: C, 34.17; H, 6.97; Cl, 7.20. Found: C, 34.37; H, 6.68; Cl, 6.72. ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 8.4 (s). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.96 (app quin, J = 7.5 Hz, 18H; $\mathrm{PCH_2C}H_3$), 1.57 (sym m, 12H; $\mathrm{P{-}C}H_2\mathrm{CH_3}$), 1.74 (t, ^{3}J(H,P) = 4.5 Hz, 4H; $\mathrm{C_2}H_4$). ^{1}H{^{31}P} NMR ($\mathrm{C_6D_6}$): δ 0.96 (t, ^{3}J(H,H) = 7.6 Hz, 18H; $\mathrm{PCH_2C}H_3$), 1.57 (q, ^{3}J(H,H) = 7.6 Hz, 12H; $\mathrm{P\text{-}C}H_2\mathrm{CH_3}$), 1.74 (s, 4H; $\mathrm{C_2}H_4$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 8.16 (s, positive in DEPT; $\mathrm{PCH_2}C\mathrm{H_3}$), 11.48 (vt, J^{vt} = 14.6 Hz, negative in DEPT; $\mathrm{P}C\mathrm{H_2CH_3}$), 17.55 (t, $^{2}J(\mathrm{C,P_{cis}})$ = 1.8 Hz, negative in DEPT; $C_2\mathrm{H_4}$).

X-ray Crystallography. Crystals of **1** were obtained at −20 °C from a concentrated toluene solution that contained complex **1** as a major component. A colorless prism with dimensions 0.5 × 0.5 × 0.4 mm was chosen for the crystallographic analysis. Crystal parameters and data collection conditions are presented in Table 1. The unit cell was obtained from 25 reflections; 3 standards were collected 28 times each, indicating a 4% change of intensity. The structure was solved by direct methods (SHELXS-93)[14] and refined by a full-matrix least-squares method based on F^2 (SHELXL-93).[15] Hydrogens were calculated from a difference Fourier map and refined in a riding mode with individual temperature factors. The final refinement for 2401 data, 111 parameters, and 3 restraints converged to R1 = 0.0544 (based on F^2), wR2 = 0.1144 (based on F^2, $I > 2\sigma(I)$) and R1′ = 0.0674 (based on F^2), wR2′ = 0.1349 (based on F^2, all data) with a goodness of fit (on F^2) of 1.080 and largest residual electron density of 2.549 e Å^{-3}. Selected bond distances and angles are listed in Tables 2 and 3. In this structure the mirror plane runs through the molecule. Atoms Ir(1), Cl(1), P(1), P(2), C(3), and C(6) sit on this mirror and have occupancies of 0.5. In addition, C(7), C(9), C(10), C(11), and their respective hydrogen atoms have occupancies of 0.5 and have been modeled along with C(8) as discretely disordered.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **1** (7 pages). Ordering information is given on any current masthead page.

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(12) For other examples of crystallographically characterized iridium−ethylene complexes see the following. (a) $\mathrm{(PPh_3)_2(PPh_2C_6H_4)Ir(C_2H_4)_2}$, d_{mean}(C−C) = 1.450(25) Å; $\mathrm{(P^iPr_3)_2(P^iPr_2CH(CH_3)CH_2)Ir(C_2H_4)_2}$, d_{mean}(C−C) = 1.430(25) Å: Perego, G.; Del Piero, G.; Cesari, M.; Clerici, M. G.; Perrotti, E. *J. Organomet. Chem.* **1973**, *54*, C51. (b) *trans*-$\mathrm{(PPh_3)_2Ir(C_2H_4)Cl}$, d(C−C) = 1.375(10) Å;[7] (c) $[\mathrm{(PMe_2Ph)_3Ir(C_2H_4)_2}][\mathrm{BF_4}]$, d_{1A}(C−C) = 1.401(25) Å, d_{2A}(C−C) = 1.427(24) Å, d_{1B}(C−C) = 1.411(22) Å, d_{2B}(C−C) = 1.431(23) Å;[9] (d) $[\mathrm{(PMe_2Ph)_3Ir(C_2H_4)Me_2}][\mathrm{BF_4}]$, d(C−C) = 1.41(5) Å: Lundquist, E. G.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1990**, *9*, 2254. (e) $\mathrm{CpIr(C_2H_4)}(\eta^2$ - $\mathrm{C_6F_6})$, d(C−C) = 1.41(3) Å: Bell, T. W.; Helliwell, M.; Partridge, M.; Perutz, R. N. *Organometallics* **1992**, *11*, 1911. (f) $\mathrm{Ir(C_2H_4)(CH_2C_6H_3(CH_3)_2)(CO)(dppe)}$, d(C−C) = 1.42(1) Å: Cleary, B. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1995**, *117*, 3510. (g) $\mathrm{(^iPr_3Sb)_2Ir(C_2H_4)_2Cl}$, d_1(C−C) = 1.42(2) Å, d_2(C−C) = 1.40(2) Å: Werner, H.; Ortmann, D. A.; Gevert, O.; *Chem. Ber.* **1996**, *129*, 411. (h) $[\mathrm{Cp^*Ir(PMe_3)(C_2H_4)(H)}][\mathrm{BF_4}]$, d(C−C) = 1.411(14) Å: Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462.

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