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Preliminary communication

(η^5-C_5H_5)($Ph_2PCH_2CH_2PPh_2$)Ru=$CH_2{}^+$ $AsF_6{}^-$. SPECTRAL CHARACTERIZATION AND MEASUREMENT OF THE BARRIER TO METHYLENE ROTATION

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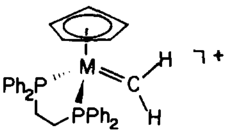
Summary

The electrophilic methylene complex (η^5-C_5H_5)($Ph_2PCH_2CH_2PPh_2$)Ru=$CH_2{}^+$ (**1**) has been characterized by ^{13}C and variable-temperature ^1H NMR spectroscopy and exhibits a vertical orientation of the methylene group with a barrier for rotation about the ruthenium–carbon double bond of 10.9 kcal/mol.

Transition metal carbene complexes of the type CpLL′Fe=CRR′$^+$ (L,L′ = CO; L = CO, L′ = phosphine; L,L′ = $Ph_2PCH_2CH_2PPh_2$); R,R′ = H, alkyl, aryl) have proved useful for examining structural details of highly electrophilic metal carbene complexes and for probing substituent and ligand effects on reactivity especially as regards cyclopropane formation via carbene transfer to alkenes [1–8]. We have begun an investigation of the ruthenium analogs of these iron systems and wish to report here the in situ generation of the parent methylene complex Cp($Ph_2PCH_2CH_2PPh_2$)Ru=$CH_2{}^+$ (**1**) together with a comparison of its spectral properties and rotational barrier with that of the iron analog Cp($Ph_2PCH_2CH_2PPh_2$)Fe=$CH_2{}^+$ (**2**) [4b].



1, M = Ru
2, M = Fe

Treatment of Cp($Ph_2PCH_2CH_2PPh_2$)RuCl [9] in benzene with excess methyllithium (8 ×, 1 h) followed by work-up and chromatography (CH_2Cl_2, alumina) gave Cp($Ph_2PCH_2CH_2PPh_2$)RuCH_3 (**3**) as a yellow powder. Recrystallization from hexane gives needles of **3** [10].

Methylene complex **1** was generated by hydride abstraction from **3**. Separate CD_2Cl_2 solutions of **3** and $(C_6H_5)_3C^+AsF_6{}^-$ were cooled to −80°C and rapidly mixed under nitrogen to give a deep red-orange solution of **1**. Characteristic of

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TABLE 1

^{13}C AND ^{1}H NMR DATA. BARRIERS TO METHYLENE ROTATION

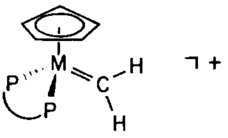
Complex	$\delta(^{13}C)$ ^{a} (ppm)	$\delta(^{1}H_a, ^{1}H_b)$ (ave) ^{b} (ppm)	$\delta(^{1}H_a),\delta(^{1}H_b)$ ^{c} (ppm)	$\Delta\delta$ (Hz) ^{d}	T_c (K)	k_{rot} (s^{-1})	$\Delta G^{\neq}_{rot}$ (kcal/mol)
1 (Ru)	311	15.6	16.7,14.2	614	250±3	1363	10.9
2 (Fe)	315	15.3	17.0,13.5	857	250±3	1905	10.8

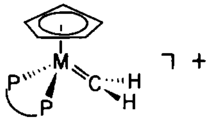
^{a} 223 K. ^{b} 298 K. ^{c} 183 K. ^{d} 250 MHz.

electrophilic transition metal methylene complexes, **1** exhibits a broad singlet for the methylene hydrogens at 15.56 ppm (298 K) and a ^{13}C resonance for C_α of 311 ppm (233 K) *.

The vertical orientation of the methylene group as depicted in **1** is confirmed by low temperature ^{1}H NMR spectroscopy which shows nonequivalent H_a and H_b protons at 16.7 ppm (br s) and 14.2 ppm (br t) (198 K). The vertical orientation is analogous to that observed in the iron analog **2** and is predicted by molecular orbital calculations [11]. Variable temperature ^{1}H NMR (250 MHz) measurements show the coalescence temperature to be 250 K corresponding to a rate for methylene rotation of 1364 s^{-1}, $\Delta G^{\neq}$ 10.9 kcal/mol. To avoid systematic errors in comparison of the methylene rotational barriers of **1** and **2**, a sample of **2**, prepared as previously reported [4b], was analyzed side-by-side with **1**. Data are summarized in Table 1.

The side-by-side comparison reveals that the barriers to rotation about the metal–carbon double bond are nearly identical for the Ru and Fe systems. The rotational barriers do not relate directly to the strength of the metal–carbon π-bond but rather to the difference in energy between the vertical, *V*, and horizontal, *H* conformations.





V H

In both conformations significant metal–carbon π-bonding obtains but with stronger π interaction in *V* relative to *H* [11]. Thus the similar barriers to rotation suggest that the differences in metal–carbon π interactions between *V* and *H* are the same for iron and ruthenium. In contrast, the analogous second and third row molybdenum and tungsten methylene complexes $Cp(CO)_2(PPh_3)M{=}CH_2{}^+$ (M = Mo, W) exhibit rotational barriers: $\Delta G^{\neq}_{Mo} \leq 6.7$ kcal/mol, $\Delta G^{\neq}_{W}$ 8.3 kcal/mol [12].

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* Complex **1** decomposes with a halflife (CD_2Cl_2 solution) at 273°C of ca. 3 h, thus isolation of the pure salt was not attempted. Thermal stabilities of 1 and 2 are similar in CD_2Cl_2 solution.

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10 (a) ^{1}H NMR (CD_2Cl_2, 250 MHz): δ 7.2–7.7 (m, 20H), 4.69 (s, 5H), 2.34 (m, 2H); 2.04 (m, 2H), -1.05 (t, 3H). ^{13}C NMR (C_6D_6, 62.89 MHz, off-resonance decoupled): δ 128–145 (complex), 82.5 (d), 27.6 (m), -23.3 (m). Anal. Found (calcd.) %: C, 66.31 (66.39); H, 5.56 (5.97); (b) The preparation of **3** has been reported previously, but no details were provided. S.G. Davies and F. Scottt, J. Organomet. Chem., 188 (1980) C41; S.G. Davies, S.D. Moon, and S.J. Simpson, Nouv. J. Chim., 8 (1984) 139.

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