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Note

Preparation, dynamic NMR behavior and X-ray structure of a novel 1:1 complex of dimethyldivinylsilane and carbonylbis(triphenylphosphine)ruthenium

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Abstract

Treatment of dihydridocarbonyltris(triphenylphosphine)ruthenium with a stoichiometric amount of styrene, followed by the addition of dimethyldivinylsilane, leads to a 1:1 complex: $[Ph_3P]_2RuCO[\eta\text{-}(CH_2{=}CH)_2Si(CH_3)_2]$. This species has been characterized fully and its structure determined by X-ray crystallography at −100°C. The structure is unsymmetrical. The two triphenylphosphine ligands are not equivalent. Similarly, while both of the C–C double bonds of the dimethyldivinylsilane ligand are π-bonded to the ruthenium center, they are also dissimilar. In solution, the ^{1}H- and ^{31}P-NMR of this complex change with temperature. At low temperature, in the ^{1}H-NMR the two methyl and the two vinyl groups bonded to silicon are each different. Similarly, in the ^{31}P-NMR spectrum the two triphenylphosphine ligands are different. At high temperature, rapid equilibration occurs averaging the spectra. The $\Delta G^{\ddagger}$ for the exchange processes for the vinyl groups in the ^{1}H-NMR and the ^{31}P-NMR are both ~12.7 kcal mol^{-1}. The $\Delta G^{\ddagger}$ for the exchange process that averages the methyl groups in the ^{1}H-NMR is ~15.2 kcal mol^{-1}. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Vinylsilanes; Dynamic NMR; Ruthenium; Polytopal rearrangement; X-ray

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1. Introduction

Dihydridocarbonyltris(triphenylphosphine)ruthenium (I) is a well-known, easily prepared complex [1] which has been shown to catalyze *ortho* alkylation reactions between acetophenone and vinylsilanes [2,3] and the copolymerization of α,ω-divinylsilanes or siloxanes with acetophenone [4,5]. Treatment of I with a stoichiometric amount of styrene at 135°C gives a quantitative yield of ethylbenzene and an active catalyst [6].

Spectroscopic examination of the activated solution by ^{31}P-NMR shows that only two triphenylphosphine groups are bonded to the ruthenium center [7] Further, addition of *ortho* acetylstyrene to the solution yields a 1:1 complex of carbonylbis(triphenylphosphine)ruthenium and *ortho* acetylstyrene whose X-ray structure has been reported [7]. In the complex, the *ortho* acetylstyrene ligand is bonded to ruthenium via a π-bond to the vinyl group and by coordination of ruthenium to the oxygen of the acetyl group.

1:1 Complexes of carbonylbis(triphenylphosphine)ruthenium and 2-phenyl pyridine or *N*-benzylideneaniline have also been reported. In these, ruthenium is bonded to the ligand by a N–Ru coordinate bond. Further insertion of ruthenium into an *ortho* C–H bond of the phenyl group yields C–Ru and Ru–H bonds [8].

2. Results and discussion

Recently we have found that the addition of dimethyldivinylsilane to a solution of an activated cata

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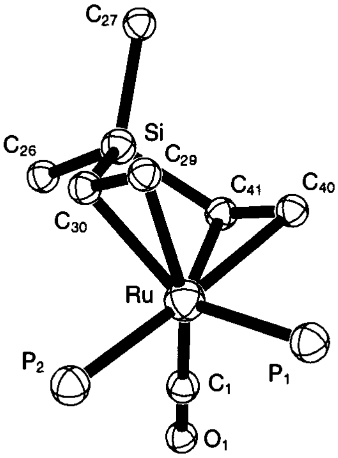

Fig. 1. X-ray structure of the complex, phenyl rings omitted.

lyst leads to an unsymmetrical 1:1 complex of dimethyldivinylsilane and carbonylbis(triphenylphosphine)ruthenium. The low-temperature (− 100°C) X-ray crystallographic structure of this complex is reported herein (Fig. 1; see Table 2 for bond lengths and bond angles). The structure of the complex is a distorted square pyramid (Fig. 2). In this, the midpoints of the C–C double bonds constitute two of the corners of the square, while P_2 and C_1 are the other corners. The ruthenium atom is slightly above the plane of the square. In this, P_1 is the apex of the square pyramid.

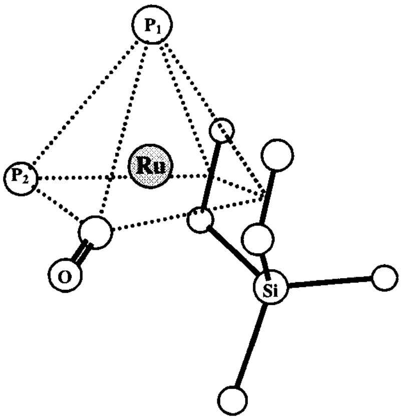

Fig. 2. Square pyramid inscribed on the atomic coordinates of the complex.

The structure is unsymmetrical. The triphenylphosphine ligands are not equivalent. Similarly, while both of the C–C double bonds of the dimethyldivinylsilane ligand are π-bonded to the Ru center they are different. The bond lengths between the Ru center and the carbons of one π-complexed double bond are shorter, Ru–C_{29} 2.208(12) Å and Ru–C_{30} 2.220(11) Å, than those between the Ru center and the other π-coordinated double bond, Ru–C_{40} 2.285(12) Å and Ru–C_{41} 2.308(12) Å. Thus, the C_{29}–C_{30} double bond is bonded more tightly to the Ru center than the C_{40}–C_{41} double bond. Consistent with this interpretation, the C_{29}–C_{30} bond length 1.41(2) Å is longer than the C_{40}–C_{41} bond length 1.37(2) Å. The latter is close to that of a free C–C double bond 1.34 Å. In comparison, the C_2–C_3 distance in the 1:1 complex of ortho acetylstyrene and carbonylbis(triphenylphosphine)ruthenium is longer 1.43 Å and the Ru–C_2 and Ru–C_3 distances are shorter 2.12 and 2.17 Å. The Ru–C, and the C–C bond lengths can be compared with those reported for the bis(styrene)bis(triphenylphosphine)ruthenium(0)[9] and similar ruthenium π-complexes [10,11], as well as with those reported for platinum π-complexes of vinylsilanes and vinylsiloxanes [12,13].

Further, this complex exhibits dynamic fluxional behavior in solution. This has been studied by ^{1}H- and ^{31}P-NMR spectroscopy. At low temperature, two signals of equal intensity which are coupled to one another are detected in the ^{31}P-NMR (δ 51.2 and 57.1), while at higher temperature these resonances broaden, coalesce ($T_c = 18$°C) and finally sharpen to a single line (δ 51.0) (Fig. 3). Analysis of these spectra on the basis of two equally populated non-equivalent sites, which undergo equilibration, yields a free energy of activation of ~ 12.4 kcal mol^{-1} for these processes [14].

Similarly, dynamic behavior is observed in the ^{1}H-NMR for the vinyl hydrogens (Fig. 4). At high temperature three signals which are coupled to one another due to the vinyl hydrogens are found at δ 0.44, 1.87 and 1.97. At low temperature these broaden, coalesce and finally split into five sharp resonances (δ − 0.15, 0.6, 1.0, 1.3 and 2.7) in a 1:1:1:1:2 intensity pattern. Kinetic analysis of these spectra yields a free energy of activation of ~ 12.7 kcal mol^{-1}. The unusually high-

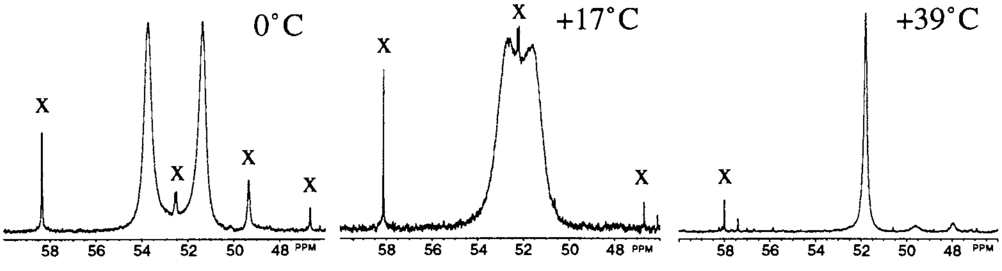

Fig. 3. ^{31}P-NMR of triphenylphosphine groups (x = impurity).

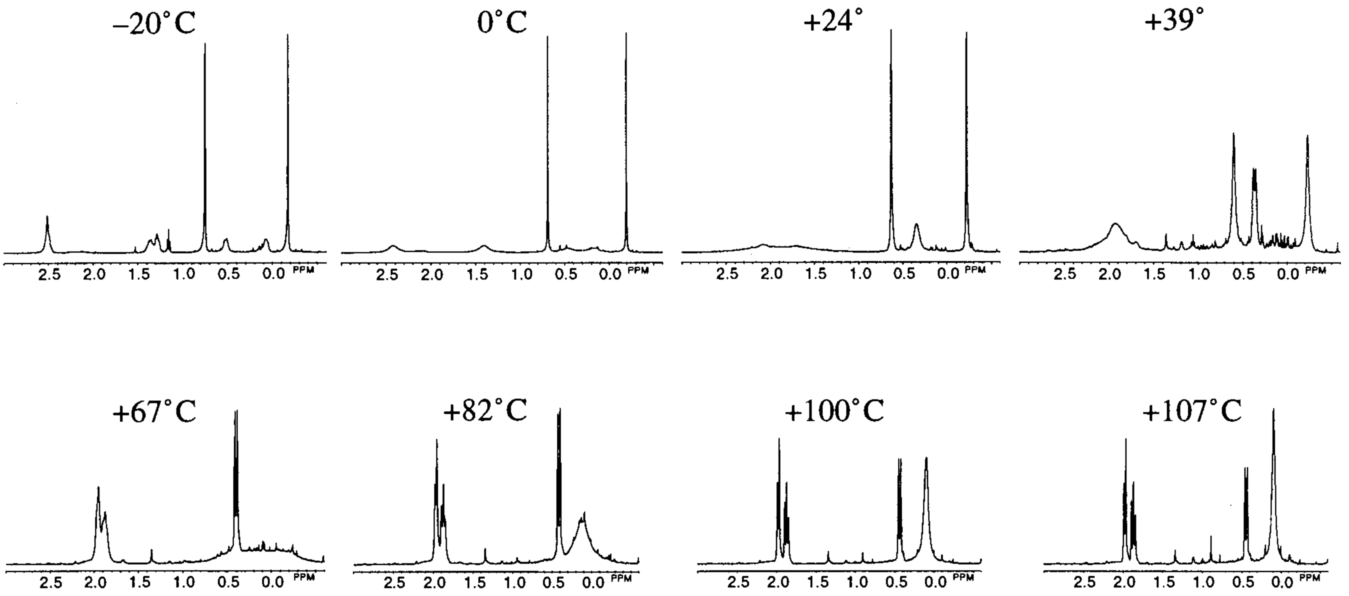

Fig. 4. ^{1}H-NMR of vinyl and Si-methyl protons.

field chemical shifts for the vinyl protons are consistent with strong bonding to the ruthenium center. These two low energy exchange processes probably occur by a polytopal rearrangement at the pentacoordinate ruthenium center [15].

At low temperature in the ^{1}H-NMR, the two methyl groups bonded to silicon give rise to two sharp singlets of equal intensity (δ -0.1 and 0.9). At higher temperature, these broaden, coalesce and then sharpen to a single resonance (δ 0.1). Kinetic analysis of this exchange process yields a free energy of activation of ~ 15.2 kcal mol^{-1}. This equilibration may occur by dissociation followed by rapid reassociation of the weakly bonded C–C double bonds to the ruthenium center.

The fact that this 1:1 complex catalyzes the copolymerization of acetophenone and α,ω-divinylsilane or siloxanes [6] suggests that π-complexation to the ruthenium center may be important in these reactions.

3. Experimental

3.1. General

^{1}H-, ^{13}C-, ^{29}Si- and ^{31}P-NMR spectra were obtained on a Bruker AMX 500 spectrometer operating in the FT mode. All spectra were run on $\sim 10\%$ w/v toluene-d_8 solutions. ^{13}C-NMR spectra were run with broad band proton decoupling. An inverse gated ^{1}H-decoupling pulse program with a 50 s delay was used to acquire ^{29}Si-NMR spectra. The central peak of the pentad of the methyl group of residual toluene-d_7 was used as an internal standard for the ^{1}H-NMR spectra. The central peak of the septet due to the methyl group of toluene-d_8 was used as an internal standard for ^{13}C-NMR spectra. ^{29}Si-NMR spectra were referenced to external TMS. ^{31}P-NMR spectra were run with broad band proton decoupling and were externally referenced to 85% phosphoric acid. IR spectra of thin films on sodium chloride plates were recorded on a Perkin–Elmer 2000 FT-IR spectrometer. Raman spectra were measured on a Bruker Equinox 55 DPY 421-NII-OEM equipped with a Nd Yag laser 1064 nm. UV spectra of diethyl ether solutions were acquired on a Shimadzu UV-260 UV–vis spectrometer.

Elemental analysis was performed by Oneida Research Services, Whitesboro, NY.

3.2. Reagents

Dimethyldivinylsilane was purchased from Gelest, and styrene was obtained from Aldrich. Dihydridocarbonyltris(triphenylphosphine)ruthenium was prepared from ruthenium trichloride trihydrate [1].

3.3. Preparation of $[Ph_3P]_2RuCO[\eta\text{-}(CH_2{=}CH)_2Si(CH_3)_2]$

Dihydridocarbonyltris(triphenylphosphine)ruthenium (1.0 g, 1.1 mmol), toluene (2 ml) and styrene (150 μl, 1.3 mmol) were heated in a test tube, equipped with a Teflon covered magnetic stir bar and sealed with a rubber septum, at 120°C for 10 min. A quantitative yield of ethylbenzene was formed. Dimethyldivinylsilane (250 ml, 1.6 mmol) was then injected into the solution. After approximately 5 min, solid material precipitated. The system was then cooled to 20°C and

10 ml of ether was added. The liquid phase was decanted and the solids were washed three times with 10 ml of ether. The solids were then dried under vacuum for 5 h. In this way, 0.78 g, 93% yield of a light yellowish powder was obtained. The powder (0.78 g) was rapidly (5 min) dissolved in refluxing toluene (5–6 ml). The solution was then rapidly cool to r.t. Over the next 2–3 h, transparent orange crystals, m.p. = 187°C, suitable for X-ray crystallography formed. ^{1}H-NMR at 107°C, fast exchange δ: 0.09 (s, 6H), 0.44 (d, 2H, $J = 14.5$ Hz), 1.87 (t, 2H, $J = 12.5$ Hz), 1.97 (d, 2H, $J = 11$ Hz), 6.99 (br. s, 18H), 7.44 (br. s, 12H). ^{1}H-NMR at -68°C, slow exchange δ: -0.15 (br. s, 1H), -0.11 (s, 3H), 0.61 (br. s, 1H), 0.89 (s, 3H), 1.00 (br. s, 1H), 1.26 (br. s, 1H), 2.74 (br. s, 2H), 6.54 (t, 2H, $J = 8$ Hz), 6.62 (t, 2H, $J = 7$ Hz), 6.73 (t, 1H, $J = 7$ Hz), 6.83 (t, 2H, $J = 7$ Hz), 6.92 (s, 9H), 6.98 (t, 3H, $J = 8$ Hz), 7.14 (t, 2H, $J = 7$ Hz), 7.60 (br. s, 6 H), 7.68 (t, 2H, $J = 8$ Hz), 8.44 (t, 2H, $J = 8$ Hz). ^{13}C-NMR δ: 213.61 (t, $C_{C=O}$, $J_{C-P} = 11.9$ Hz), 139.07, 134.65, 134.25, 134.98, 128.80, 127.96, 127.82, 53.00, 29.75, 4.41, -1.93. ^{31}P-NMR δ: 51.18 (d, 1P, $J_{P-P} = 16$ Hz), 57.12 (d, 1P, $J_{P-P} = 16$ Hz). ^{31}P-NMR at 67°C, fast exchange δ: 51.02 (s, 2P). ^{29}Si-NMR at 20°C δ: -5.19, -5.15, -5.10 (1:2:1 ratio). ^{29}Si-NMR at -59°C δ: -3.82, -3.74 (1:1 ratio). IR ν: 3056, 1884, 1585, 1479, 1433, 1310, 1241, 1184, 1086, 834, 743, 696, 555, 521 cm^{-1}. Raman ν: 3168, 3142, 3095, 3061, 3024, 3004, 2978, 2959, 2938, 2903, 2888, 1879, 1586, 1232, 1159, 1090, 1031, 1004, 685, 622, 609, 560, 467, 394, 360, 267, 160, 112, 99 cm^{-1}. UV λ_{max} (ε): 337 (8240), 248 (18630). Elemental Anal. Calc. for $C_{43}H_{42}OP_2RuSi$: C, 67.42; H, 5.54; P, 8.09; Ru, 13.19. Found: C, 67.30; H, 5.44; P, 7.43; Ru, 13.17.

Table 1
Crystal data and structure refinement for $[Ph_3P]_2RuCO[\eta\text{-}(CH_2{=}CH)_2Si(CH_3)_2]$

Empirical formula	$C_{43}H_{42}OP_2RuSi$
Formula weight	765.87
Temperature (K)	193(2)
Wavelength (Å)	1.54178
Crystal system	Monoclinic
Space group	$P2_1/n$ (#14)
Unit cell dimensions	
a (Å)	10.368(3)
b (Å)	20.748(2)
c (Å)	16.849(2)
α (°)	90
β (°)	98.29(2)
γ (°)	90
V (Å^3)	3586.6(12)
Z	4
$D_{calc.}$ (g cm^{-3})	1.418
Absorption coefficient (mm^{-1})	4.955
F(000)	1584
Crystal size (mm)	0.20 × 0.35 × 0.45
Theta range for data collection (°)	3.40–47.50°
Index ranges	$-9 \leq h \leq 9$, $-13 \leq k \leq 19$, $-16 \leq l \leq 16$
Reflections collected	4310
Independent reflections	3276 [$R_{int} = 0.0426$]
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	3274/0/213
Goodness-of-fit on F^2	1.040
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0630$, $wR_2 = 0.1659$
R indices (all data)	$R_1 = 0.0835$, $wR_2 = 0.1924$
Largest difference peak and hole (e A^{-3})	0.637 and -0.882

Table 2
Bond lengths (Å) and angles (°) for $[Ph_3P]_2RuCO[\eta\text{-}(CH_2{=}CH)_2Si(CH_3)_2]$

Bond lengths (Å)			
Ru–C_1	1.848(12)	Ru–P_2	2.353(3)
Ru–C_{29}	2.208(12)	Si–C_{41}	1.838(12)
Ru–C_{30}	2.220(11)	Si–C_{30}	1.846(12)
Ru–C_{40}	2.285(12)	C_{29}–C_{30}	1.41(2)
Ru–C_{41}	2.308(12)	C_{40}–C_{41}	1.37(2)
Ru–P_1	2.401(3)		
Bond angles (°)			
C_1–Ru–P_1	104.8(4)	P_1–Ru–C_{29}	97.3(3)
C_1–Ru–P_2	87.1(4)	P_1–Ru–C_{30}	134.4(3)
C_1–Ru–C_{40}	96.6(5)	P_2–Ru–C_{40}	176.0(3)
C_1–Ru–C_{41}	80.1(5)	P_2–Ru–C_{41}	145.5(3)
C_1–Ru–C_{29}	157.8(5)	P_2–Ru–C_{29}	91.1(3)
C_1–Ru–C_{30}	120.8(5)	P_1–Ru–P_2	98.93(12)
P_2–Ru–C_{30}	85.0(3)	C_{30}–Ru–C_{40}	91.8(4)
C_{29}–Ru–C_{30}	37.1(4)	C_{30}–Si–C_{41}	96.5(5)
C_{40}–Ru–C_{41}	34.7(4)	C_{29}–C_{30}–Si	119.2(9)
C_{29}–Ru–C_{40}	84.9(4)	C_{40}–C_{41}–Si	125.3(9)
C_{30}–Ru–C_{41}	74.7(4)	Ru–C_{30}–Si	94.7(5)
C_{29}–Ru–C_{41}	89.1(4)	Ru–C_{41}–Si	92.0(5)
P_1–Ru–C_{40}	81.6(3)	C_{26}–Si–C_{27}	108.1(7)
P_1–Ru–C_{41}	115.2(3)		

4. X-ray structure analysis

A crystal was mounted on a glass fiber with oil and placed in a Siemens P4/RA diffractometer for data collection at -100°C. The annular settings of well-centered reflections indicated a monoclinic unit cell whose dimensions are given in Table 1. Four monitor reflections indicated no significant decrease in intensity during data collection, which was carried out with Cu–K_α radiation up to a 2θ maximum of 90°. The position of the Ru atom and the seven atoms attached to it were obtained from a Patterson map with crystallographic package SHELX-86 [16]. The rest of the non-hydrogen atoms were subsequently located from a series of structure factor/difference Fourier calculations [17]. The important bond lengths and angles in the 1:1 complex are given in Table 2. The X-ray analysis was completed with several cycles of full-matrix least-squares refinements, with anisotropic thermal parameters assigned to all atoms. The final agreement factor $R(F) = 6.3\%$ for 3274 reflections.

5. Supplementary material

Tables giving crystal data and refinement details, positional and thermal parameters, and bond distances and angles for the 1:1 complex discussed in this paper have been deposited with the Cambridge Crystallographic Data Centre, CDDC Nos. 118424. Copies of the data can be obtained, free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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