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Tetraphenylborate Coordination Chemistry. Synthesis, Solid-State and Solution Characterization, and Properties of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3$ and $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_3BPh\}(O_3SCF_3)_2$: The First Examples of a Tetraphenylborate Anion Acting as a 12- or 18-e Donor to Metal Centers[†,1]

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$\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3$ (**3**) and $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_3BPh\}(O_3SCF_3)_2$ (**4**) have been synthesized by reaction of $(C_2H_4)_2Rh(\eta^6\text{-}PhBPh_3)$ with in situ generated $Rh(C_2H_4)_2(O_3SCF_3)$ (1 or 2 mol, respectively). **3** and **4** are the first examples of a tetraphenylborate anion bridging two and three metal centers, respectively. $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3$ has been characterized in the solid state by X-ray diffraction (crystals of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot(CH_3)_2CO$ are monoclinic, space group $P2_1/n$; $a = 13.050(1)$ Å, $b = 14.805(2)$ Å, $c = 19.736(4)$ Å, $\beta = 70.71(1)°$, $Z = 4$, $V = 3599$ Å^3) and in solution by means of ^{1}H and ^{13}C NMR spectroscopy. Complex **3** shows, in solution, at room temperature, a complicated fluxional behavior involving the rotation of the coordinated ethylene molecules around the metal–olefin bond axis, the rotation of the $(C_2H_4)_2Rh$ fragments around the respective Rh–arene bond vector, and the interconversion of its enantiomeric forms upon rotation of the BPh_4^- phenyl rings around the B–C bonds. The energy barrier at 301 K relative to the rotation of the olefin molecules has been measured as being $\Delta G^{\ddagger}(301\ K) = 57.7\ kJ\ mol^{-1}$. Complex **4** has been characterized in solution by ^{1}H NMR spectroscopy. In solution of poorly coordinating solvents it has been shown to be partially dissociated into **3** and $Rh(C_2H_4)_2(O_3SCF_3)$. The dissociation is temperature dependent. The first example of a tetraphenylborate anion transfer between two metal centers is also described.

Introduction

The ability of the tetraphenylborate anion, BPh_4^-, to act as a ligand to an electron-deficient metal center through one of the phenyl rings is documented in the literature by a few complexes,[1-13] most of which have been structurally characterized.[2,5-11] When the coordinated phenyl ring acts as a 6-e donor, it has been observed to deviate only slightly from planarity[5,7,10] or to assume a "boat conformation" (normal[2] or inverted[8]) according to the nature of the metal atom and the ancillary ligands.

In principle, there is no reason for limiting to one the number of the BPh_4^- anion phenyl rings acting as a ligand toward a metal center: provided that electron and steric requirements are fulfilled, the tetraphenylborate anion can act as a 24-e donor. Very recently, in fact, a report appeared in the literature concerning the synthesis of $\{[Cp^*Ru(\eta^6\text{-}Ph)]_4B\}(O_3SCF_3)_3$ ($Cp^* = \eta\text{-}C_5Me_5$), that was characterized in solution by ^{1}H and ^{13}C NMR techniques, but not in the solid state.[14,15] We report here the synthesis, the structural characterization (in the solid state and/or in solution), and the properties of both $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3$ and its higher homologue $\{[(C_2H_4)_2\text{-}$

[†] Dedicated to Professor Adriano Sacco on his 70th birthday.

[1] Parts of this work have been presented at the following international and national meetings: (a) Aresta, M.; Di Mauro, M.; Quaranta, E.; Tommasi, I. Interfaces in Metal Complex Chemistry. *Book of Abstracts*, International Symposium, University of Rennes, Rennes, France, July 1989; p PB26. (b) Albinati, A.; Aresta, M.; Olivieri, V.; Quaranta, E. *Proceedings of the XXVIIIth International Conference on Coordination Chemistry*, Gera, Germany, August 1990; Vol. 2, pp 4–65. (c) Albinati, A.; Aresta, M.; Fragale, C.; Quaranta, E.; Tommasi, I. *Proceedings of CISCI*, CISCI 91, Chianciano Terme, Italy, October 1991; Vol. II, p 648.

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Table I. Chemical Shifts [δ (ppm), CD_2Cl_2, 293 K] of the Tetraphenylborate Protons in Some Mononuclear η^6-BPh_4Rh Complexes

complex	$H_{o,\eta^6\text{-}Ph}$	$H_{m,\eta^6\text{-}Ph}$	$H_{p,\eta^6\text{-}Ph}$	H_{o,BPh_3}	H_{m,BPh_3}	H_{p,BPh_3}
(bpy)Rh(η^6-$PhBPh_3$)[a]	5.96	5.59	*b*	*b*	*b*	*b*
(diphos)Rh(η^6-$PhBPh_3$)[c]	6.23	5.47	6.31	7.09	6.89	6.86
$(C_2H_4)_2$Rh(η^6-$PhBPh_3$)	6.44	6.07	6.98	7.32	7.14	7.02

[a] Reference 24. [b] $H_{p,\eta^6\text{-}Ph}$, H_{m,BPh_3}, H_{o,BPh_3}, and H_{p,BPh_3} give overlapping multiplets in the 6.79–7.01 ppm region. No exact location of these signals was made. [c] Reference 21.

Rh(η^6-Ph)]$_3$BPh}$(O_3SCF_3)_2$, the first examples of a BPh_4^- anion bridging two and three metal centers, respectively.

Results and Discussion

Synthesis and Characterization of $(C_2H_4)_2$Rh(η^6-$PhBPh_3$) (1) and Rh$(C_2H_4)_2(O_3SCF_3)$ (2). $(C_2H_4)_2$Rh(η^6-$PhBPh_3$)[17] (1) can be easily prepared by treating Cramer's complex $[Rh(C_2H_4)_2Cl]_2$,[18] dissolved in toluene, with 2 mol of sodium tetraphenylborate, as shown in eq 1. 1 was obtained as a yellow microcrystalline compound stable in air.

$$[Rh(C_2H_4)_2Cl]_2 + 2NaBPh_4 \rightarrow \underset{\mathbf{1}}{2(C_2H_4)_2Rh(\eta^6\text{-}PhBPh_3)} + 2NaCl \quad (1)$$

The IR spectrum of 1 shows characteristic absorptions at 1480 and 1388 cm^{-1} due to C–C skeletal vibrations of uncoordinated and coordinated phenyl rings, respectively, and bands at 1220, 1210, 986, 831, and 820 cm^{-1} due to the coordinated ethylene molecules.[19]

The ^1H NMR spectrum of 1 in CD_2Cl_2 shows the expected high-field shift for the protons of the coordinated phenyl ring, as usually encountered in M(η^6-arene)[20] and other M(η^6-BPh_4) complexes.[2,3,10,21] The spectrum of the coordinated phenyl ring can be interpreted on the basis of a first-order approximation,[21] and both the signal multiplicities and the integral values show that the resonances at 6.44 (d, 2 H) and 6.07 ppm (t, 2 H) are due to the ortho and meta protons ($H_{o,\eta^6\text{-}Ph}$ and $H_{m,\eta^6\text{-}Ph}$), respectively. The signal of the para proton ($H_{p,\eta^6\text{-}Ph}$) is located at 6.98 ppm (m, 1 H) and is partially masked by the resonance of the para protons of the uncoordinated phenyl rings. The ethylene protons give two broad signals at 3.15 and 1.85 ppm, that suggests a fluxional behavior involving the coordinated ethylene molecules.[22]

In Table I the chemical shifts of both the coordinated and uncoordinated phenyl ring protons of 1 are compared with those observed in the same conditions[23] for other mononuclear L_2Rh(η^6-$PhBPh_3$) complexes we have prepared [L_2 = diphos,[8,21] bpy (2,2′-bipyridyl)[24]]. The inspection of these data, as well as of those available in the literature,[2,3] shows that the chemical shift of each set of protons of both the coordinated and uncoordinated phenyl rings is strongly dependent on the nature of the ancillary ligands in the coordination sphere of rhodium. We note, however, that the smaller upfield shift of the coordinated phenyl ring protons in 1 well matches the poorer σ-donor and the higher π-acceptor ability of the ethylene ancillary ligands.[25]

The ^{13}C NMR spectrum (THF-d_8) shows a net separation of the signals due to the uncoordinated and coordinated phenyl carbons: upon coordination to Rh the resonances of the phenyl ring carbons (ortho, meta, para) are upfield shifted[26] by about 20–25 ppm and split in doublets by coupling with Rh (see the Experimental Section). The J_{C-Rh} coupling constants range around 1–3 Hz;[21] as a comparison, J_{C-Rh} in the range 3–4 Hz are found for $(C_5H_5)Rh^{III}$ and $(C_5H_5)Rh^I$ species.[27] The value of the coupling constant for Rh–C can be related to the σ- and π-character of the arene–metal bond:[28] our data indicate that in 1 the phenyl–metal bond seems to have a strong π-character. A single signal at 50.28 ppm (d, J_{C-Rh} = 12.7 Hz) is exhibited by the coordinated ethylene carbons. Both the position and the observed value of J_{C-Rh} are within the range usually found for the coordinated olefin.[28,29] Unfortunally, the low solubility in most solvents and the thermal instability at temperatures higher than room temperature prevented a more complete investigation of the NMR behavior of 1.

The reaction of Cramer's complex with AgO_3SCF_3 in THF at 240 K produces Rh$(C_2H_4)_2(O_3SCF_3)$[30] (2) (eq 2) that can be isolated as a yellow solvated complex, unstable in the solid state under dinitrogen or ethylene, as it looses the coordination solvent also at 250 K. Aromatic solvents cannot be used in the isolation of this complex, as they coordinate easily to Rh, displacing the weakly coordinated $CF_3SO_3^-$ anion. This property has been used for the synthesis of the title compounds.

$$[Rh(C_2H_4)_2Cl]_2 + 2AgO_3SCF_3 \rightarrow \underset{\mathbf{2}}{2Rh(C_2H_4)_2(O_3SCF_3)} + 2AgCl \quad (2)$$

Synthesis and Solid-State Characterization of {[$(C_2H_4)_2$Rh(η^6-Ph)]$_2$BPh$_2$}O_3SCF_3 (3). When a THF

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[17] This complex was first prepared by an independent route by Osborn (see ref 3). We report here the complete IR and NMR characterization.

[18] Cramer, R. *Inorg. Chem.* **1962**, *1*, 722.

[19] The bands assigned to the coordinated ethylene molecules are absent in the spectrum of (diphos)Rh(η^6-$PhBPh_3$) [see ref 8; diphos = 1,2-bis(diphenylphosphino)ethane].

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[23] The chemical shift of the coordinated phenyl ring protons is very sensitive to the nature of the solvent.[21]

[24] (a) Semeraro, L. Doctor Thesis, University of Bari, 1987. (b) Aresta, M.; Quaranta, E. In press.

[25] The shielding of η^6-$PhBPh_3$ protons is dependent on several factors such as, for instance, the σ-donor or π-acceptor properties of the ancillary ligands, the chemical shift anisotropy of the ligands or of particular functional groups in the ligand molecules, the equilibrium conformational geometry of the overall complex, and the occurrence of fluxional processes. It is not trivial to evaluate the relative weight of these factors in determining the shielding of each set of BPh_4^- protons in such systems, and thus, it is quite difficult to fully rationalize, from a simple qualitative point of view, the data of Table I.

[26] Graves, V.; Lagowski, J. S. *Inorg. Chem.* **1976**, *15*, 577.

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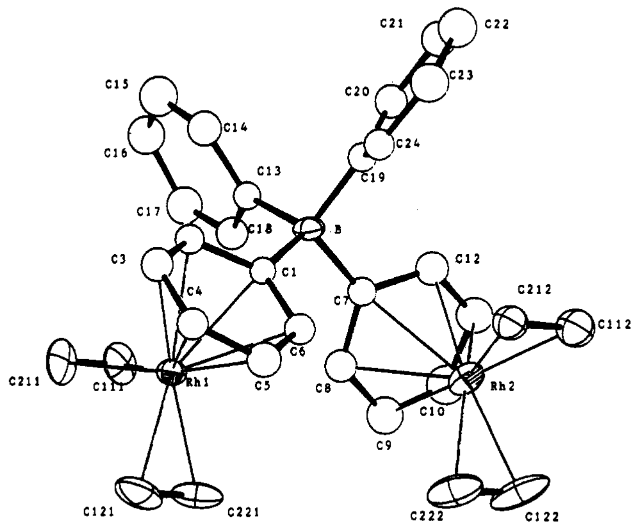

Figure 1. ORTEP drawing of the structure of the $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}^+$ (3^+) cation.

solution of 1 (1 mol) is treated at 273 K under dinitrogen with 1 mol of 2 (eq 3: 2 is prepared in situ under ethylene),

$$\underset{1}{(C_2H_4)_2Rh(\eta^6\text{-}PhBPh_3)} + \underset{2}{Rh(C_2H_4)_2(O_3SCF_3)} \to \underset{3}{\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3} \quad (3)$$

a yellow microcrystalline compound of formula $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot 0.5THF$ is isolated. Recrystallization of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot 0.5THF$ from CH_2Cl_2/*n*-pentane affords pure $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3$ (3).

The IR spectrum of 3 in Nujol shows characteristic bands at 1395 (skeletal vibration of the coordinated phenyls), 1275 [$\nu_{as}(SO_3)$], 1223 [$\nu_s(CF_3)$], 1170 [$\nu_{as}(CF_3)$], 1030 [$\nu_s(SO_3)$],[31] 823–805 (=CH_2 rocking), and 630, 571, and 517 cm^{-1} (SO_3 deformation).[32] These features suggest that the $CF_3SO_3^-$ anion is not coordinated to Rh in the solid state.

$\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot 0.5THF$ was recrystallized from anhydrous acetone to afford crystals of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot(CH_3)_2CO$ suitable for X-ray structural analysis.

An ORTEP view of the molecular structure of the $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}^+$ cation, 3^+, is given in Figure 1, while selected bond lengths and angles are listed in Table II.

The compound consists of discrete dimeric cations, $CF_3SO_3^-$ counterions, and clathrathed acetone molecules; the structure is held together by van der Waals forces.

In the cation each rhodium atom is coordinated to one of the phenyl rings of a bridging tetraphenylborate anion. The coordination around each metal center is completed by two ethylene molecules.

Table II. Selected Bond Distances (Å) and Angles (deg) for $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot(CH_3)_2CO$ [$3\cdot(CH_3)_2CO$]

Rh1–C111	2.154(8)	Rh2–C7	2.396(7)
Rh1–C211	2.149(8)	Rh2–C8	2.302(7)
Rh1–C121	2.143(7)	Rh2–C9	2.199(9)
Rh1–C221	2.146(7)	Rh2–C10	2.325(9)
Rh1–C1	2.370(6)	Rh2–C11	2.295(9)
Rh1–C2	2.258(6)	Rh2–C12	2.241(8)
Rh1–C3	2.308(7)	$(C\text{–}C)_{ethylene}$[a]	1.40(4)
Rh1–C4	2.325(7)	$(C\text{–}C)_{phenyl}$[a]	1.41(4)
Rh1–C5	2.266(8)	B–C[a]	1.640(8)
Rh1–C6	2.329(7)	Rh1–Cm1[b]	2.03
Rh2–C112	2.196(8)	Rh1–Cm2[b]	2.04
Rh2–C212	2.144(7)	Rh2–Cm3[b]	2.06
Rh2–C122	2.141(8)	Rh2–Cm4[b]	2.07
Rh2–C222	2.186(8)		
Cm1–Rh1–Cm2[b]	94.8	C7–B–C13	105.7(6)
Cm3–Rh2–Cm4[b]	94.4	C7–B–C19	110.0(5)
C1–B–C7	111.4(6)	C13–B–C19	110.0(6)
C1–B–C19	108.2(6)	C2–Rh1–C5	77.6(3)
C1–B–C13	111.7(6)	C7–Rh2–C10	76.1(3)

[a] Average value. [b] Cm are the midpoints of the C=C bonds.

The rhodium ethylene distances [average 2.162(2) Å] are in the range found for other complexes[33] (2.13–2.16 Å) as are the C=C distances at 1.40(4) Å (average).

The distances between the Rh atoms and the planes of the coordinated phenyl rings are comparable, being 1.81 and 1.80 Å, respectively; the separations between the metals and the carbon atoms of the rings are in the range 2.20–2.40 Å, somewhat shorter than those found in $Rh(diphos)(\eta^6\text{-}PhBPh_3)$[8] (2.28–2.44 Å).

The interaction of the tetraphenylborate with the metal centers affects both the geometry and the conformation. The two phenyl rings η^6-bonded deviate slightly from planarity, resulting in a boat conformation with atoms C2, C5 and C9, C12 pointing toward the metal. These deviations, albeit small [0.05(1) Å from the least squares plane for C2 and C5, 0.5(1) and 0.7(2) Å for C9 and C12, respectively] are significant (using a χ test) and consistent with the geometry found in other structures.[7-10] Moreover, the atoms deviating from planarity are those with the shortest distances to the rhodium atoms; i.e. Rh1—C2 and Rh1—C5 are 2.258(6) and 2.266(8) Å, and Rh2—C9 and Rh2—C12 are 2.199(9) and 2.241(8) Å, respectively. This may correspond to a certain "localization" in M—C(phenyl) bonds, in keeping with the tendency of Rh centers to achieve a pseudo-square-planar coordination, the coordination plane being defined by these two carbon atoms and the midpoint of the C=C ethylene bonds.

There are no significant differences in the B–C separations [average 1.640(8) Å], while the C–B–C angles [in the range 105.7(5)–111.7(6)°] deviate from the ideal tetrahedral values as a result of the coordination. The dihedral angle between the planes defined by the coordinated phenyl rings is 65°, with the angles involving the remaining rings ranging from 56 to 96°, indicating, as expected, a change from the conformation of an uncoordinated tetraphenylborate where values in the range 70–125° are found.[34] We also note that the interplanar angles between the two coordinated and the uncoordinated rings are 92 and 96° (see also later the NMR discussion).

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[31] There is some uncertainty in the literature about the assignment of the ν_{as} and ν_s for SO_3 and CF_3 groups in triflate anion compounds. In fact, in AgO_3SCF_3 the following assignments have been made: 1270 [$\nu_{as}(SO_3)$], 1237 [$\nu_s(CF_3)$], 1167 [$\nu_{as}(CF_3)$], 1043 cm^{-1} [$\nu_s(SO_3)$] (Burger, H.; Burczyk, K.; Blaschette, A. *Monatsh. Chem.* **1970**, *101*, 102). However, for NaO_3SCF_3 the bands at 1280 and 1240 cm^{-1} have been assigned to $\nu_{as}(SO_3)$ and $\nu_s(SO_3)$, respectively, whereas the bands at 1175 and 1035 cm^{-1} have been attributed respectively to $\nu_s(CF_3)$ and $\nu_{as}(CF_3)$ (Miles, M. B.; Doyle, G.; Cooney, R. P.; Tobias, R. S. *Spectrochim. Acta, Part A*, **1969**, *25*, 1515).

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[33] Orpen, G. A.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

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Characterization of {[$(C_2H_4)_2Rh(\eta^6\text{-Ph})]_2BPh_2$}-$O_3SCF_3$ (3) in Solution. Like 1, 3 also seems to be a fluxional system. In fact, the ethylene protons give, at 293 K in CD_2Cl_2, two broad signals at 3.27 and 2.07 ppm, at lower fields than the ethylene protons of 1. Furthermore, the ^{13}C NMR spectrum of 3 (293 K, $CDCl_3$) shows only one signal for the ethylene carbons (51.19 ppm), which is split into a doublet by Rh–C coupling ($J_{C\text{-}Rh}$ = 12.1 Hz).

The most relevant structural features disclosed by the solid-state investigations are also retained in solution. As a matter of fact, both the ^1H and ^{13}C NMR spectra of 3 show two sets of signals, proving that two of the tetraphenylborate phenyl rings are coordinated to Rh.

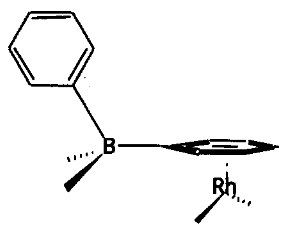
In the ^1H spectrum (CD_2Cl_2, 293 K), the signals due to the protons of the coordinated phenyls are found at 7.26 (t, $H_{p,\eta^6\text{-}(Ph)_2}$),[35] 6.52 (d, 4 H, $H_{o,\eta^6\text{-}(Ph)_2}$), and 6.36 ppm (t, 4 H, $H_{m,\eta^6\text{-}(Ph)_2}$, $^3J_{H_m\text{-}H_o} \cong {}^3J_{H_m\text{-}H_p}$ = 6.38 Hz), whereas the resonances of the uncoordinated phenyl ring protons are observed at 7.40 (d, 4 H, H_{o,BPh_2}, $^3J_{H_o\text{-}H_m}$ = 6.84 Hz), 7.24 (m, H_{m,BPh_2}), and 7.13 ppm (m, 2 H, H_{p,BPh_2}).

In the ^{13}C NMR spectrum of 3 (293 K, $CDCl_3$) the signals due to carbon atoms of the uncoordinated phenyls are observed at 135.60, 126.93, and 125.07 ppm,[36] whereas those due to the corresponding carbons of the coordinated phenyl rings are, as expected, upfield shifted and found as doublets at 108.67, 104.88, and 103.09 ppm.[36] Unfortunately, despite the high number of transients, we have not been able to detect the signal due to the carbon atom of the triflate ion and the resonances due to the ipso carbons of both the coordinated and uncoordinated phenyl rings.[37]

A few features of the NMR spectra of 3 require a detailed discussion.

Both the ^1H and ^{13}C NMR spectra, at 293 K, clearly show that the uncoordinated phenyl rings, as well as the $(C_2H_4)_2Rh(\eta^6\text{-Ph})$ moieties, are equivalent: this suggests that the {[$(C_2H_4)_2Rh(\eta^6\text{-Ph})]_2BPh_2$}$^+$ cation, 3^+, has a C_2 molecular symmetry in solution.[38] The conformational analysis of 3^+ leads to the discovery of several conformations having this symmetry. Their inspection by using framework molecular models (FMM) allows us to conclude that 3^+ maintains, in solution, a conformation analogous to that found in the solid state (see *1*; for clearness sake, only one member of each structural unit, which 3^+ consists of, is shown). In this conformation the plane of each free phenyl ring is perpendicular (see the solid-state structure) to the mean plane of one of the coordinated phenyl rings. Moreover, as emphasized in *1*, each $(C_2H_4)_2Rh$ group is anti-oriented with respect to the uncoordinated phenyl bisecting the phenyl ring which the rhodium atom is coordinated to.

As a result of the C_2 symmetry the cation 3^+ must exist in two enantiomeric forms $3a^+$ and $3b^+$ (see Scheme I).



1

The two enantiomeric forms can be interconverted by rotation around the B–C single bonds, and on this basis, they can be considered as conformational enantiomers. As emphasized in Scheme I, this process also exchanges positions diastereotopically related and, in principle, not equivalent: 3 and 5, 2 and 6, 8 and 12, 9 and 11, for the two $(C_2H_4)_2Rh(\eta^6\text{-Ph})$ moieties; 14 and 18, 15 and 17, 20 and 24, 21 and 23 for the two uncoordinated phenyl rings. As in the ^1H and ^{13}C NMR spectra only one signal is found for the ortho as well as the meta nuclei (^1H, ^{13}C) of both free and η^6-phenyl rings; the interconversion of the two enantioconformers is very fast at room temperature (293 K) on the NMR time scale. In fact, it is worth noting that the two ortho nuclei, as well as the meta ones, of the same phenyl ring are diastereotopic and, consequently, not equivalent. However, they can become spectroscopically enantiotopic and, therefore, equivalent through the same process which interconverts an enantioconformer in the other one, if the conformer interconversion rate is fast on the NMR time scale.

We also note that a fast rotation of each $(C_2H_4)_2Rh$ group around the $(\eta^6\text{-Ph})$–Rh bond axis is possible. The rotation of M–L_n fragments around an η^6-arene ligand–metal bond vector is a dynamic process well-known in the literature,[39] and the energy barrier is usually very low [about 2 kJ/mol for $(C_6H_6)Cr(CO)_3$[39a]], unless exceptional steric or electronic factors are operating.[39c,g] The internal rotation energy barrier is predicted to be very low in $L_2Rh(\eta^6\text{-PhBPh}_3)$ complexes,[40a] and the structural data for 3 do not show any special steric hindrance for the internal rotation of the $(C_2H_4)_2Rh$ fragment. Thus, it seems fairly reasonable to assume that the rotation of the $(C_2H_4)_2Rh$ fragments is also free in 3. Perturbation theory and extended Huckel calculations[40] have allowed the statement of a clear dependence of the arene ligand ring puckering on the conformational arrangement of the M–L_n unit in these systems. It should be noted that conformation *2* should stabilize a distortion of the η^6-arene ligand like that found in $[(MeO)_3P]_2Rh(\eta^6\text{-PhBPh}_3)$,[2] whereas conformation *3* should favor an opposite arene ring deformation.[40a] Therefore, the fast rotation of the $(C_2H_4)_2Rh$ fragments should result in the time-averaged planarity of the coordinated phenyl rings and, consequently, in the equivalence of the two $(C_2H_4)_2Rh(\eta^6\text{-Ph})$ moieties.

---

(35) The accurate location of the signal at 7.26 ppm ($H_{p,\eta^6\text{-}(Ph)_2}$) has been accomplished by means of homonuclear decoupling experiments. In fact, by irradiating the triplet at 6.36 ppm the signal at 7.26 ppm collapses to a singlet showing that $^4J_{H_p\text{-}H_o}$ is too small to be resolved. Moreover, selective decoupling on the signal at 7.26 ppm converts the triplet at 6.36 ppm into a doublet, whereas it does not produce any simplification of multiplicity for the resonance at 6.52 ppm.

(36) No further attempt to define in greater detail the assignment of these signals was made.

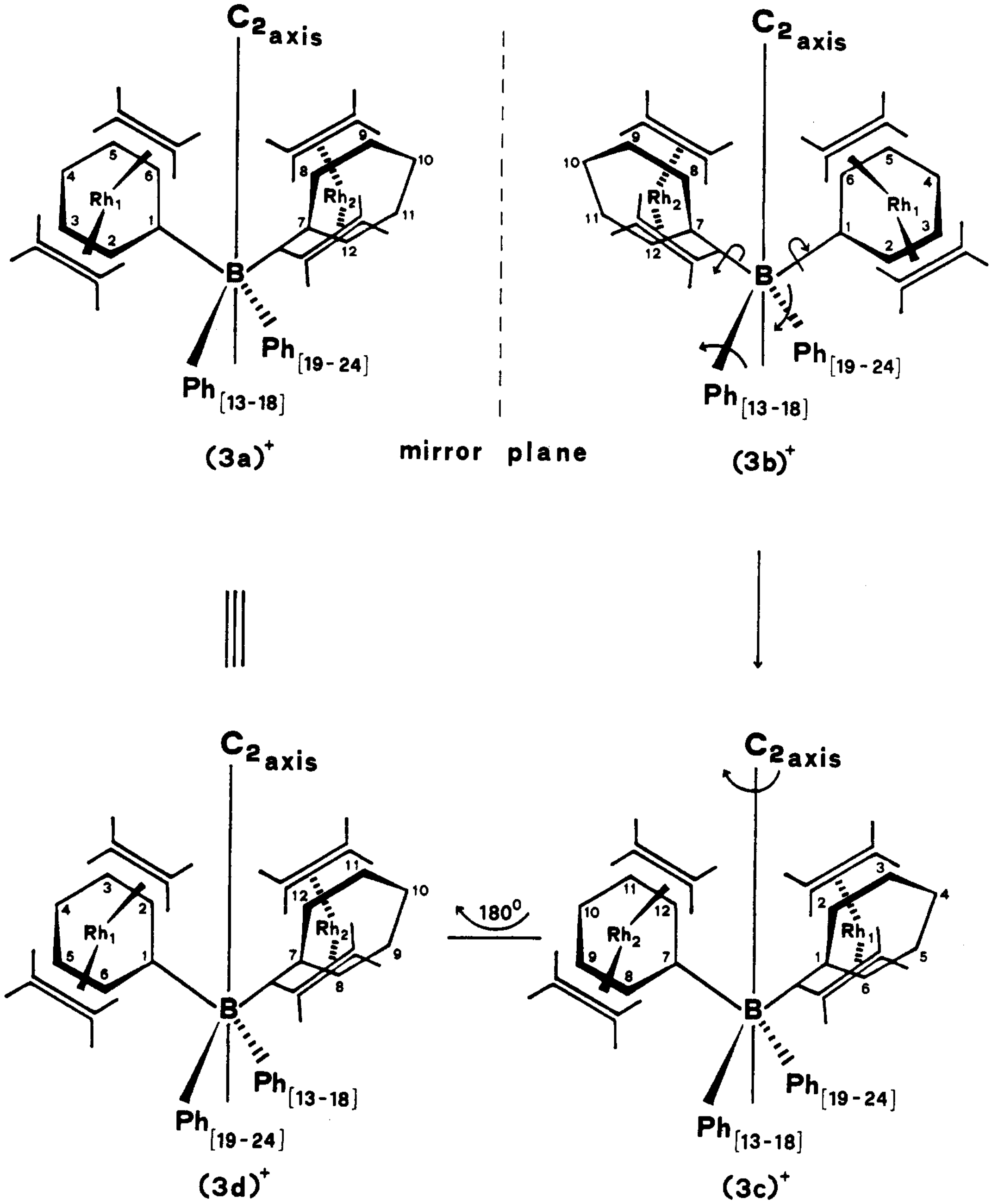
(37) The lack of these signals can, in part, be due to the poor solubility of **3** in the solvent used. The utilization of $CDCl_3$ as solvent was suggested by the need that the 40–60 ppm spectrum region had to be free from solvent resonances in order to locate correctly the resonances of the coordinated ethylene carbons.[28,29]

(38) C_{2v} symmetry can be excluded for cation 3^+ because the conformational arrangements consistent with this symmetry group can be shown to be very crowded.

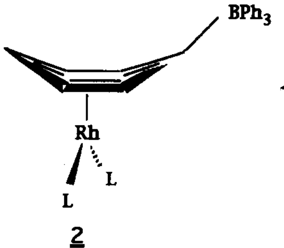
(39) (a) Chiu, N. S.; Schafer, L.; Seip, R. J. *J. Organomet. Chem.* **1975**, *101*, 331. (b) Delise, P.; Allegra, G.; Magnaschi, E. R.; Chierico, A. *J. Chem. Soc., Faraday Trans.* **1975**, *71*, 207. (c) Acampora, M.; Ceccon, A.; Dal Fara, M.; Giacometti, G.; Rigatti, J. *J. Chem. Soc., Perkin Trans. 2* **1977**, *2*, 483. (d) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149. (e) Hunter, G.; Weakley, J. R.; Mislow, K.; Wong, M. G. *J. Chem. Soc., Dalton Trans.* **1986**, 577. (f) Hu, X.; Duchowscki, J.; Pomeroy, R. K. *J. Chem. Soc., Chem. Commun.* **1988**, 362. (g) Pomeroy, R. K.; Harrison, D. J. *J. Chem. Soc., Chem. Commun.* **1989**, 661. (h) Chudek, J. A.; Hunter, G.; Mackay, R. L.; Farber, G.; Weissemsteiner, W. *J. Organomet. Chem.* **1989**, *377*, C69.

(40) (a) Albright, T. A.; Hoffmann, R.; Tse, Y.-Ching; D'Ottavio, T. *J. Am. Chem. Soc.* **1979**, *101*, 3812. (b) Radanovich, L. J.; Koch, F. J.; Albright, T. A. *Inorg. Chem.* **1980**, *19*, 3373.

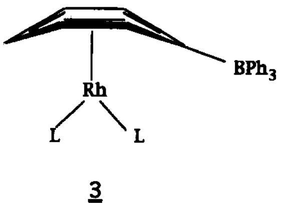
Scheme I. Schematic Representation of the Enantio Conformers 3a$^+$ and 3b$^+$ and Their Interconversion through Rotation around the B–C Bonds^a



^{a} The Ph(19–24) and Ph(13–18) phenyl rings are not shown in detail. In 3a$^+$ and 3b$^+$, they are, respectively, perpendicular to the mean plane of Ph(1–6) and Ph(7–12). In 3c$^+$ [note that 3c$^+$ = 3d$^+$ ≡ 3a$^+$] Ph(19–24) is orthogonal to the mean plane of Ph(7–12), while Ph(13–18) is perpendicular to that of Ph(1–6).



2



3

Indirect experimental evidence for the internal rotation of the $(C_2H_4)_2Rh$ groups comes from the inspection of the VT-^{1}H spectrum of 3 in the region of the ethylene protons. We shall discuss these results later when we deal with the fluxional behavior of the coordinated ethylene molecules in complex 3.

Dynamic Behavior of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3$. VT-^{1}H NMR experiments (200 MHz, CD_2Cl_2,[41] 193–310 K) have been performed in order to clarify the nature of the fluxional behavior of 3. In Figure 2 we have reported the upfield region (1.5–4.0 ppm) of the ^{1}H spectrum of 3 in the 253–301 K range.

The two broad signals (3.27 and 2.07 ppm) observed at 293 K coalesce at 301 K (coalescence temperature), and one very broad signal (not shown in Figure 2), approxi-

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[41] The utilization of CD_2Cl_2 as solvent was made necessary by the solubility of 3 in this medium and the poor coordinating power of dichloromethane. However, this choice precluded the possibility to perform measurements at temperatures higher than 310 K. Indeed, we have ascertained that such a limitation is fictitious because of the chemical behavior of 3 in solution above 310 K (Aresta, M.; Quaranta, E. Paper submitted for publication).

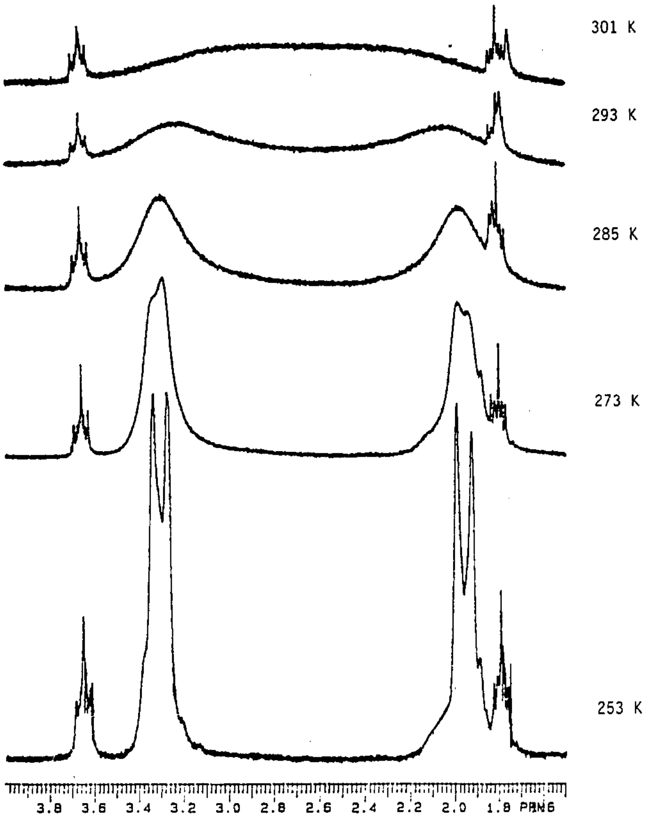

Figure 2. VT-^{1}H NMR spectrum of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3$ (**3**) (200 MHz, CD_2Cl_2, 253–301 K, ethylene region). The multiplets centered at 3.7 and 1.8 ppm are due to crystallization THF (see Experimental Section).

mately centered at 2.65 ppm, can be observed at 310 K,[42] the maximum temperature which may be attained due to the solvent used. This result clearly shows that at temperatures higher than 301 K all 16 ethylene protons exchange fast on the ^{1}H time scale and become equivalent. Lowering the temperature below 293 K causes the two broad signals at 3.27 and 2.07 ppm to become two pseudodoublets centered respectively at 3.31 and 1.96 ppm (spacing 13 Hz), which both correctly integrate to 8 H. No further decoalescence is observed in the ^{1}H spectrum by lowering the temperature to 193 K.

We can exclude the fact that the equilibration of all ethylene protons involves the dissociation of the coordinated ethylene molecules. In fact, experiments performed under an ethylene atmosphere in conditions of both intermediate (293 K, 200 MHz) and faster (310 K, 90 MHz) exchange rate (on the NMR time scale) induce no shift of coordinated and free ethylene signals.[43] Further evidence also comes from the ^{13}C spectrum (50.3 MHz, $CDCl_3$, under dinitrogen) of **3** at 310 K, under conditions of rapid ethylene proton equilibration. At that temperature the ethylene carbon resonance is still a doublet (51.21 ppm, $J_{C\text{-}Rh}$ = 11.7 Hz) due to ethylene carbon–rhodium coupling. This ensures that the dynamic process responsible for the equilibration of all 16 ethylene protons of **3**, at temperatures not higher than 310 K, does not disturb the coordination of the ethylene molecules and has an intramolecular character.

The equivalence of the ethylene protons at temperatures higher than 301 K requires a more complex explanation and can be rationalized by taking into account the following internal rotational processes: (i) interconversion of the two enantiomeric forms of **3** by rotation of the phenyl rings around the C–B bonds; (ii) rotation of the ethylene molecules around the Rh–olefin bond axis; (iii) rotation of the $(C_2H_4)_2Rh$ fragments around the respective (η^6-Ph)–Rh bond axis.

Let A_1, B_1, C_1, D_1 and A_2, B_2, C_2, D_2 be the protons of the two ethylene molecules (1 and 2, respectively) coordinated to Rh1, and A_3, B_3, C_3, D_3 and A_4, B_4, C_4, D_4 those of molecules 3 and 4, respectively, bonded to Rh2 (Scheme II). The existence of the C_2 axis entails the equivalence of the ethylene molecules 1–4, and 2 and 3; moreover, it also correlates the A_1, B_1, C_1, D_1 and A_2, B_2, C_2, D_2 protons to A_4, B_4, C_4, D_4 and A_3, B_3, C_3, D_3, respectively. The equivalence of the following protons can be stated.

$$A_1 \equiv A_4 \qquad A_2 \equiv A_3$$

$$B_1 \equiv B_4 \qquad B_2 \equiv B_3$$

$$C_1 \equiv C_4 \qquad C_2 \equiv C_3$$

$$D_1 \equiv D_4 \qquad D_2 \equiv D_3$$

Ethylene molecules 1 and 2 are diastereotopic, as well as 3 and 4. Therefore, a diastereotopic relation must also correlate A_1, B_1, C_1, D_1 and A_3, B_3, C_3, D_3 to A_2, B_2, C_2, D_2 and A_4, B_4, C_4, D_4, respectively. The interconversion of

$$A_1 \equiv A_2 \qquad A_3 \equiv A_4$$

$$B_1 \equiv B_2 \qquad B_3 \equiv B_4$$

$$C_1 \equiv C_2 \qquad C_3 \equiv C_4$$

$$D_1 \equiv D_2 \qquad D_3 \equiv D_4$$

the two enantioconformers **3a**$^+$ and **3b**$^+$ upon internal rotation of the coordinated and free phenyl rings around their respective B–C bonds exchanges the diastereotopic protons and, under the conditions in which such a motion occurs fast on the ^{1}H time scale, renders them enantiotopic. Therefore, when the symmetry properties of **3**$^+$ are considered and the possibility of internal rotation around the B–C bonds is assumed, the equivalence of the following ethylene protons can be shown:

$$A_1 \equiv A_2 \equiv A_3 \equiv A_4$$

$$B_1 \equiv B_2 \equiv B_3 \equiv B_4$$

$$C_1 \equiv C_2 \equiv C_3 \equiv C_4$$

$$D_1 \equiv D_2 \equiv D_3 \equiv D_4$$

Under conditions of rapid (on the ^{1}H time scale) rotation of the ethylene molecules around the Rh–olefin bond, also

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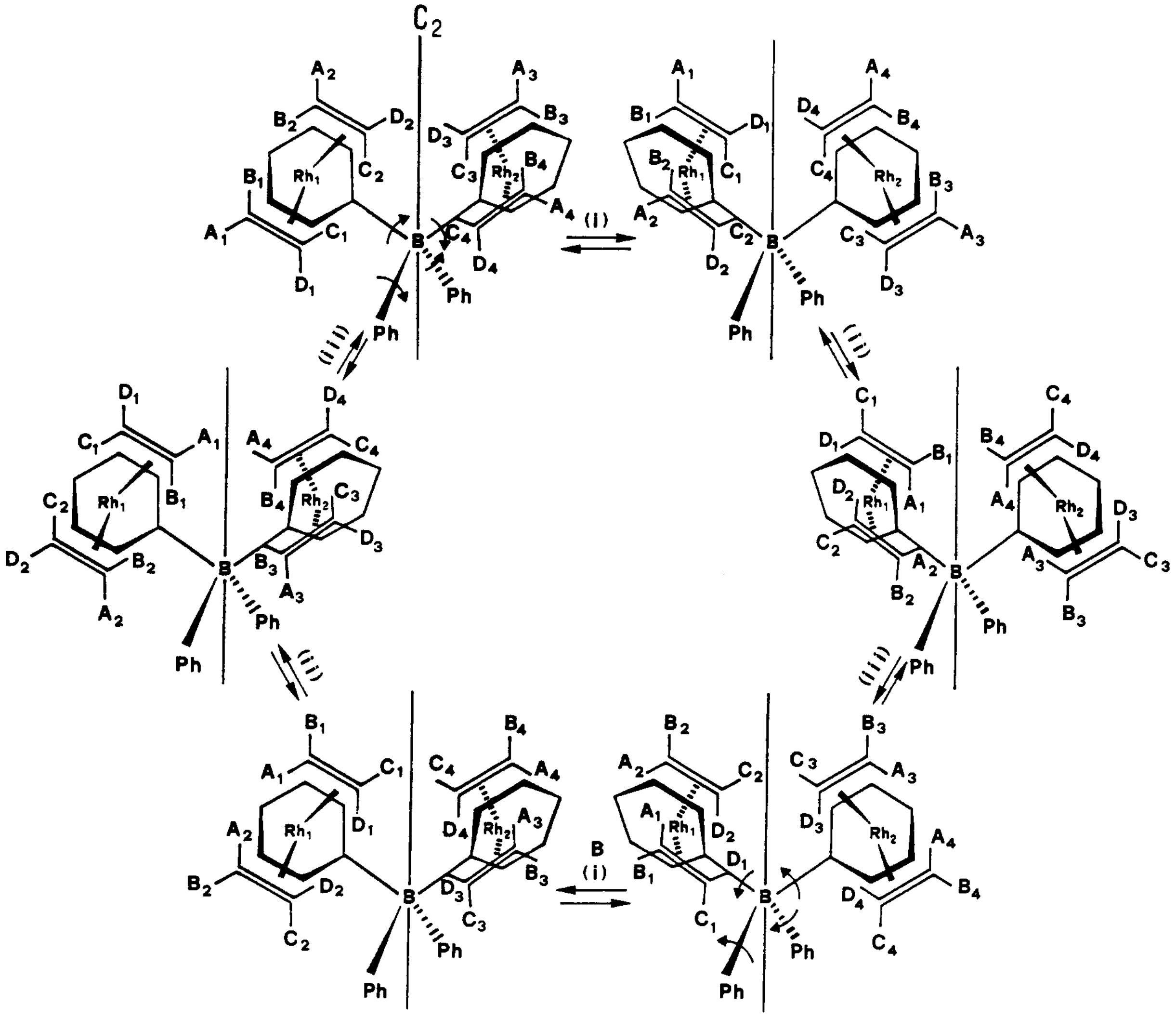
[42] The resonance at 2.65 ppm is still quite broad also when the ^{1}H spectrum was measured at 90 MHz, at the same temperature (310 K).

[43] This result also shows that no coordinated–free ethylene exchange seems to occur when **3** is exposed to an ethylene atmosphere under the experimental conditions here described. This is not surprising considering that the two Rh atoms are 18-e metal centers: for these systems the coordinated–free ethylene exchange should involve a dissociative pathway (see also refs 44).

Scheme II. Equilibration of the Ethylene Protons for the 3^+ Cation: (i) Interconversion of the Enantiomeric Forms of 3^+ through Rotation of the Phenyl Rings around the B–C Bonds; (ii) Rotation of the Ethylene Molecules around the Rh–Olefin Axis; (iii) Rotation of the $(C_2H_4)_2Rh$ Moieties around the Respective (η^6-Ph)–Rh Bond Axis



the following protons become equivalent:

A_1 and C_1 A_3 and C_3

B_1 and D_1 B_3 and D_3

A_2 and C_2 A_4 and C_4

B_2 and D_2 B_4 and D_4

The 16 ethylene protons fall, thus, into two noninterconvertible sets of eight:

$$A_1 \equiv C_1 \equiv A_2 \equiv C_2 \equiv A_3 \equiv C_3 \equiv A_4 \equiv C_4$$

$$B_1 \equiv D_1 \equiv B_2 \equiv D_2 \equiv B_3 \equiv D_3 \equiv B_4 \equiv D_4$$

We note that each set consists of pairs of trans protons from distinct ethylene molecules. Moreover, these considerations show that no less than two signals should be expected in the ^{1}H spectrum of **3**, if only the internal rotations i and ii are taken into account.

The equivalence of all 16 ethylene protons requires that the rotation of the $(C_2H_4)_2Rh$ fragments around the respective (η^6-Ph)–Rh bond vectors, (iii), must be considered. This process can exchange the following protons

A_1 and D_2 A_3 and D_4

D_1 and A_2 D_3 and A_4

B_1 and C_2 B_3 and C_4

C_1 and B_2 C_3 and B_4

and allows us to explain the equilibration of all the ethylene protons at temperatures higher than 301 K (see also (Scheme II).

The energy barriers for each of the internal rotational motions above examined should be, in principle, different, and three different coalescence temperatures should be measured from the VT-^{1}H spectrum of **3**, each one connected with one of the processes (i)–(iii). In this study we have been able to measure only one of them, which is related to a dynamic process having an energy barrier $\Delta G^{\ddagger}$(301 K) of 57.7 kJ mol^{-1}. This value agrees well with those found for the internal rotation of olefins in other Rh complexes,[22,39d,44b,c] and on this basis, we believe that the dynamic process responsible for the coalescence at 301 K is the rotation of the ethylene ligand around the Rh–olefin bond axis. Therefore, the ^{1}H spectrum observed at 253 K (or, also, at 193 K) is not the limit spectrum but corresponds to a dynamic situation in which only the ethylene rotational motion is frozen. The foregoing discussion allows us to show that freezing this internal motion causes all the ethylene protons to fall into the following noninterchangeable sets of eight protons:

$$A_1 \equiv D_1 \equiv A_2 \equiv D_2 \equiv A_3 \equiv D_3 \equiv A_4 \equiv D_4$$

$$B_1 \equiv C_1 \equiv B_2 \equiv C_2 \equiv B_3 \equiv C_3 \equiv B_4 \equiv C_4$$

Each set is composed of pairs of cis protons from distinct ethylene molecules; furthermore, the members of the (A_i, D_i) set are all "outside" protons, while the (B_i, C_i) set consists only of "inside" protons. An AA′XX′ spectrum should be expected for such a system of nuclei. Accordingly, the ^{1}H spectrum of **3** at 253 K is consistent with these conclusions. As the inside protons of a coordinated olefin are more strongly shielded than the outside ones by a second olefin coordinated to the same metal center,[44] we assign the signal at 3.31 ppm (8 H) to the protons of the (A_i, D_i) set, whereas the doublet at 1.96 ppm (8 H) is attributed to the (B_i, C_i) proton set.

It is well-known that utilization of high magnetic fields can be of help in studying very fast dynamic processes. VT-^{1}H NMR experiments at 500 MHz are in progress in order to study in greater detail the rotational processes (i) and (iii) and to evaluate quantitatively their energy barriers.

Stability of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3$. In the solid state, **3** is stable for a long time, even in the presence of oxygen or moisture. No remarkable change was observed in the IR spectrum of a solid sample of **3** exposed to the atmosphere for 3 days; moreover, the elemental analysis of this sample is still consistent with the $C_{33}H_{36}BF_3O_3Rh_2S$ formula.

In solution, the stability of **3** strongly depends on the nature of the solvent; for example, solutions of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot0.5THF$ in CH_3CN, a coordinating solvent, show values of molar conductivity, Λ_M, which are time-dependent. For a fresh-prepared 2.16×10^{-3} M solution of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot0.5THF$ in CH_3CN, Λ_M increases from 124.7 to 137.7 S cm^2 mol^{-1} within 1 h.[45] Analogously, a 1:10 dilution of this solution (2.16×10^{-4} M), causes the Λ_M rise from 181.5 to the limit value of 237.9 S cm^2 mol^{-1} within 15 h at 293 K.

These data show that, in coordinating solvents, a conversion of the complex occurs. The limit value found for a 2.16×10^{-4} M solution of **3** in CH_3CN (237.9 S cm^2 mol^{-1}) is remarkably higher than that expected for CH_3CN solutions of 1:1 electrolytes of comparable concentration[47] and suggests that in coordinating solvents **3** converts into more than one ionic species according to eq 4. The coordinating solvent displaces the BPh_4^- anion from both the Rh centers, leading to two new 1:1 electrolytes.[49] An analogous behavior has been observed by us and other authors on similar systems.[11,21]

$$\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3 \xrightarrow{S} [Rh(C_2H_4)_2S_m]BPh_4 + [Rh(C_2H_4)_2S_n]O_3SCF_3 \quad (4)$$

S is a coordinating solvent

Transfer of the Tetraphenylborate Anion between Two Metal Centers. The attempts to prepare the complex $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)][(diphos)Rh(\eta^6\text{-}Ph)]BPh_2\}O_3SCF_3$ by a way analogous to the one affording **3** have been unsuccessful. The reaction (in THF) of **2** with (diphos)Rh(η^6-PhBPh$_3$) does not lead to the formation of the asymmetric dinuclear tetraphenylborate complex $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)][(diphos)Rh(\eta^6\text{-}Ph)]BPh_2\}O_3SCF_3$. We have isolated from the reaction mixture the compound $(C_2H_4)_2Rh(\eta^6\text{-}PhBPh_3)\cdot THF$, whose formation suggests that reaction 5 occurs. In eq 5 the formal transfer of tetraphenylborate anion from a (diphos)Rh moiety to a $(C_2H_4)_2Rh$ fragment is involved: *this reaction is the first example of a tetraphenylborate anion transfer between two metal centers.*

$$(diphos)Rh(\eta^6\text{-}PhBPh_3) + Rh(C_2H_4)_2(O_3SCF_3) \rightarrow (C_2H_4)_2Rh(\eta^6\text{-}PhBPh_3)\cdot THF + Rh(diphos)(O_3SCF_3) \quad (5)$$

$(C_2H_4)_2Rh(\eta^6\text{-}PhBPh_3)\cdot THF$ has been isolated as a pure compound and characterized by means of elemental analysis and IR spectroscopy.[50] The second product of reaction 5, Rh(diphos)(O_3SCF_3), could not be isolated in a very pure form.[51]

We can reasonably rule out that the BPh_4^- transfer reaction (eq 5) involves, as a preliminary step, the dissociation of the BPh_4^- anion from the (diphos)Rh moiety. As a matter of fact, the NMR spectra (^{1}H, ^{11}B, ^{13}C) of (diphos)Rh(η^6-PhBPh$_3$)[21] and measurements of electrolytic conductivity in solutions of this complex[8] do not produce any experimental evidence for the dissociation of the arene ligand, at least in the conditions used for the reaction. More likely, the attack of **2** to the tetraphenylborate anion of (diphos)Rh(η^6-PhBPh$_3$) occurs when the anion is still coordinated to the (diphos)Rh fragment. Two possibilities can be envisaged: (1) compound **2** attaches to the same phenyl ring bearing the (diphos)Rh unit (more plausibly, from the open side); (2) the Rh–

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[44] (a) Cramer, R. *J. Am. Chem. Soc.* **1964**, *86*, 217. (b) Cramer, R.; Kline, J. B.; Roberts, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 2519. (c) Cramer, R.; Mrowca, J. J. *Inorg. Chim. Acta* **1971**, *5*, 528.

[45] Λ_M(CH_3CN, 10^{-3} M) ranges within 120–160 S cm^2 mol^{-1} for 1:1 electrolytes.[46]

[46] Walton, R. A. *Quart. Rev.* **1965**, *19*, 126.

[47] For Et_4NBr in CH_3CN the value of the A constant in the Kohlrausch equation [$\Lambda = \Lambda_0 - A\sqrt{C}$] is equal to 460.[48] Considering this value as typical for 1:1 electrolytes in CH_3CN, we can estimate the change of Λ_M for a 1:1 electrolyte in CH_3CN upon 1:10 dilution (from 2.16×10^{-3} to 2.16×10^{-4} M). The calculations show that $\Delta\Lambda_M$ should range around 10–20 S cm^2 mol^{-1}. This means that, for a 1:1 electrolyte in CH_3CN, Λ_M($\cong 10^{-4}$ M) ranges from 130 to 180 S cm^2 mol^{-1}. The limit value of 237.9 S cm^2 mol^{-1} is far higher than the acceptable maximal value.

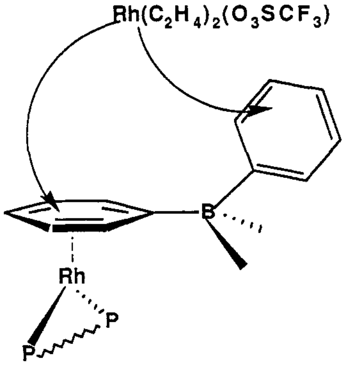
[48] Fowles, G. W. A.; Green, P. T. *J. Chem. Soc. A* **1967**, 1869.

[49] The poor coordinating ability of the triflate anion is well documented in the literature.[32b] However, it cannot be excluded that covalent species, such as $Rh(C_2H_4)_2(\eta^n\text{-}O_3SCF_3)(S)$ (n = 1 or 2) or $[Rh(C_2H_4)_2(O_3SCF_3)]_2$, are present, at low concentration, in equilibrium with $[Rh(C_2H_4)_2S_n]O_3SCF_3$.

[50] The IR spectrum of $(C_2H_4)_2Rh(\eta^6\text{-}PhBPh_3)\cdot THF$ does not show remarkable differences with respect to that of **1** except for two more bands at 1067 (s, sh) and 910 cm^{-1} (m, br), suggesting the presence of crystallization THF. It is worth noting that recrystallization of **1** from very diluted THF solutions, at 253 K, affords $(C_2H_4)_2Rh(\eta^6\text{-}PhBPh_3)\cdot THF$.

[51] The fractionated crystallization of the mother solution led to the isolation of a phosphorus-containing raw material which shows properties similar to those found for **2** (IR: 1310, 1275, 1175, and 1035 cm^{-1}).

Scheme III. Possible Pathways for the Tetraphenylborate Anion Transfer from the (diphos)Rh Moiety of (diphos)Rh(η^6-PhBPh$_3$) to the (C$_2$H$_4$)$_2$Rh Group of Rh(C$_2$H$_4$)$_2$(O$_3$SCF$_3$)



triflate complex binds one of the uncoordinated phenyls (see Scheme III). In this case, the attack of 2 should lead to the formation of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)][(diphos)Rh(\eta^6\text{-}Ph)]BPh_2\}O_3SCF_3$ which, however, could not be isolated even when the reaction of (diphos)Rh(η^6-PhBPh$_3$) with 2 was carried out at low temperature (253 K). The experimental finding that the analogous reaction of 1 with 2 affords 3, leads us to single out the attack of 2 on one of the uncoordinated phenyls of (diphos)Rh(η^6-PhBPh$_3$) as the most probable pathway.[52]

Synthesis, Characterization, and Properties of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_3BPh\}(O_3SCF_3)_2$ (4). The reaction of 1 (1 mol) with 2 mol of 2 prepared in situ (eq 2) gives a yellow microcrystalline compound of formula $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_3BPh\}(O_3SCF_3)_2$ (4) (eq 6), stable in air, very soluble in acetone, and moderately soluble in chlorinated solvents.

$$\underset{\mathbf{1}}{(C_2H_4)_2Rh(\eta^6\text{-}PhBPh_3)} + \underset{\mathbf{2}}{2Rh(C_2H_4)_2(O_3SCF_3)} \rightarrow \underset{\mathbf{4}}{\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_3BPh\}(O_3SCF_3)_2} \quad (6)$$

Compound 4 has been characterized by elemental analyses, IR, and ^{1}H NMR (see Experimental Section).

The ^{1}H spectrum of 4 (at 293 K, in CD$_2$Cl$_2$, Figure 3) clearly shows that three (C$_2$H$_4$)$_2$Rh units are η^6-coordinated to three phenyls of the tetraphenylborate anion. As for compound 3, the signals of the ethylene ligands are broad (3.25 and 2.20 ppm) and coalesce at the temperature 301 K. In Table III we report the chemical shift of BPh$_4^-$ protons of 4, compared with the chemical shift of the corresponding protons of the two lower homologues, 1 and 3. The phenyl protons of 3 and 4 exhibit their resonances at lower fields than the corresponding protons of 1. The net average positive charge on each of the Rh atoms of 3 and 4 can be responsible for the greater deshielding of the phenyl protons of 3 and 4 with respect to 1. The data in Table III also show that, except for the ortho protons, deshielding is of greater importance for the protons of the coordinated phenyl rings, accounting, thus, for the quite surprising lower-field resonance of both $H_{p,\eta^6\text{-}(Ph)_2}$ and $H_{p,\eta^6\text{-}(Ph)_3}$ with respect to the H_{p,BPh_2} and $H_{p,BPh}$ protons, respectively. It should be noted that in complex 1 the corresponding protons, $H_{p,\eta^6\text{-}Ph}$ and H_{p,BPh_3}, are almost isochronous.

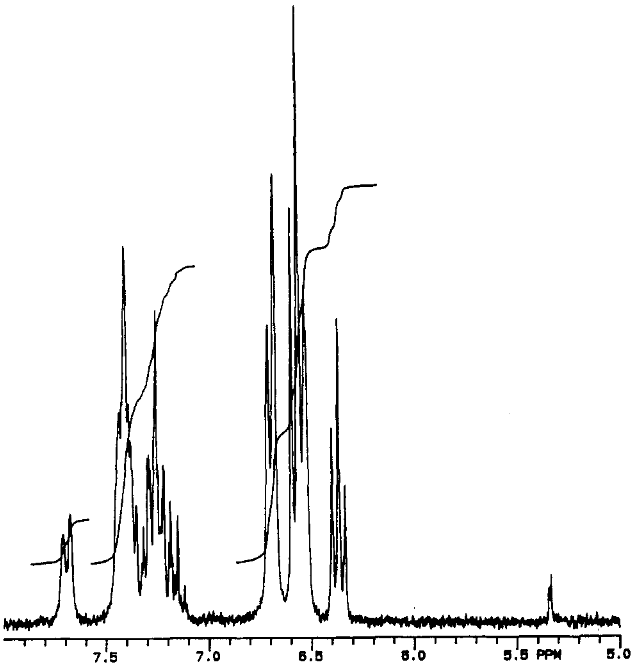


Figure 3. ^{1}H NMR spectrum of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_3BPh\}(O_3SCF_3)_2$ (4) (200 MHz, CD$_2$Cl$_2$, 293 K, aromatic region).

Compound 4 partially dissociates in solution to give 3 and 2 according to eq 7. This is clearly shown by the features of the ^{1}H spectrum of 4 that presents the signals

$$\underset{\mathbf{4}}{\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_3BPh\}(O_3SCF_3)_2} \rightleftharpoons \underset{\mathbf{3}}{\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3} + \underset{\mathbf{2}}{Rh(C_2H_4)_2(O_3SCF_3)} \quad (7)$$

due to the dinuclear complex 3 (see, for example, in Figure 3 the signals at 6.36 and in the range 7–7.3 ppm). The dissociation is temperature-dependent: α, as measured using the ^{1}H NMR data, is 38% at 294 K and 43% at 301 K. In our opinion, the dissociation is a consequence of the steric hindrance around the boron atom, that causes the decoordination of one of the three Rh moieties.

However, this behavior makes difficult the isolation of pure tetranuclear $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_4B\}(O_3SCF_3)_3$ that we have obtained contaminated with 4.

This is the first study on such a dissociative equilibrium for multinuclear tetraphenylborate metal complexes. It is worth noting that the behavior shown by the Rh systems seems to be different from that shown by $\{[(Cp^*Ru(\eta^6\text{-}Ph)]_4B\}(O_3SCF_3)_3$,[14] for which no decoordination of Cp*Ru moieties from the tetraphenylborate anion has been reported to occur in solution, despite the steric hindrance of the Cp* ligands.

Conclusions

Complexes 3 and 4 are the first examples of a tetraphenylborate anion bridging two and three metal centers. These data complete the literature reports and allow us to conclude that the BPh$_4^-$ anion can act as a 6-, 12-, 18-, and 24-e donor, very selectively.

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[52] The larger sterical encumberment due to the diphos ligand might account for the different stabilities of the $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)][(diphos)Rh(\eta^6\text{-}Ph)]BPh_2\}^+$ and 3$^+$ cations.

Table III. Chemical Shifts [δ (ppm), CD_2Cl_2, 293 K] of the Coordinated and Uncoordinated Phenyl Ring Protons of $(C_2H_4)_2Rh(\eta^6\text{-}PhBPh_3)$ (1), $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3$ (3), and $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_3BPh\}(O_3SCF_3)_2$ (4)[a]

complex	$H_{o,\eta^6\text{-}(Ph)_n}$	$H_{m,\eta^6\text{-}(Ph)_n}$	$H_{p,\eta^6\text{-}(Ph)_n}$	H_{o,BPh_m}	H_{m,BPh_m}	H_{p,BPh_m}
1 (n = 1, m = 3)	6.44	6.07	6.98	7.32	7.14	7.02
3 (n = m = 2)	6.52 (0.08)	6.36 (0.29)	7.26 (0.28)	7.40 (0.08)	7.24 (0.10)	7.13 (0.11)
4 (n = 3, m = 1)	6.69 (0.25)	6.56 (0.49)	7.39 (0.41)	7.69 (0.37)	7.40 (0.16)	7.34 (0.32)

[a] The values in parentheses measure the deshielding (in ppm) of BPh_4^- protons of **3** or **4** with respect to the corresponding protons of **1**.

Compound **3** has been characterized in the solid state by X-ray diffraction. In solution it shows a complex fluxional behavior involving the rotation of the coordinated ethylene molecules around the metal–olefin bond axis, the rotation of the $(C_2H_4)_2Rh$ fragments around the respective Rh–arene bond vector, and enantiomeric interconversion through rotation of the BPh_4^- phenyl ring around the B–C bonds. The stability of **3** in solution is dependent on the nature of the solvent: coordinating solvents displace the BPh_4^- anion, leading to ionic species.

Complex **4** has been characterized in solution by ^1H NMR spectroscopy. Already in solutions of poorly coordinating solvents it undergoes partial dissociation to **3** and $Rh(C_2H_4)_2(O_3SCF_3)$ due to steric hindrance around the boron atom.

We have also documented the first case of a BPh_4^- anion transfer between two metal centers.

These data are helpful to understand the chemistry of the tetraphenylborate anion in metal systems and are relevant to the behaviour of BPh_4^- metal complexes in catalysis.

Experimental Section

General Comments. Unless otherwise stated, all reactions and manipulations were conducted under a dinitrogen atmosphere by using vacuum-line techniques. All solvents were dried as described in the literature and stored under dinitrogen. $[Rh(C_2H_4)_2Cl]_2$, $NaBPh_4$, and AgO_3SCF_3 were commercial products (Aldrich). Ethylene (99.7% minimum) was from Matheson. (diphos)$Rh(\eta^6\text{-}PhBPh_3)$ was prepared as previously reported.[8,21]

Infrared spectra were obtained with a Perkin-Elmer 883 spectrophotometer. NMR spectra were run on a Varian XL-200 (at 200 MHz for ^1H and 50.3 MHz for ^{13}C) or on a Varian EM390 instrument (for proton experiments at 90 MHz). Chemical shifts are reported in ppm vs TMS. Electrolytic conductivity measurements were made on a WTW conductivity meter apparatus.

Synthesis of $(C_2H_4)_2Rh(\eta^6\text{-}PhBPh_3)$ (1). $NaBPh_4$ (1.157 g, 3.38 mmol) in toluene/methanol (5:1 v/v, 24 mL) was added, under an ethylene stream, to a filtered, cold (263 K) solution of $[Rh(C_2H_4)_2Cl]_2$[53] (0.7334 g, 1.89 mmol) in toluene (54 mL). The reaction mixture was stirred for 30 min at 263 K and, then, filtered. The yellow solid isolated by filtration was washed with toluene, with distilled water until chlorine-free washing solutions were obtained, and then with cold acetone and, finally, dried in vacuo. Yield of **1**: 0.946 g, 1.98 mmol, 59% vs $NaBPh_4$. **1** is slightly soluble in THF, CH_2Cl_2, and acetone but poorly soluble in $CDCl_3$, aromatics, methanol, and diethyl ether. Anal. Calcd for $C_{28}H_{28}BRh$: C, 70.32; H, 5.90. Found: C, 70.26; H, 5.82. IR (Nujol, KBr disks, cm^{-1}): 1480 (m-s), 1425 (m-s), 1388 (m-s), 1220 (m), 1210 (m-w), 986 (m), 831 (m-w), 820 (m-w). ^1H NMR (CD_2Cl_2, 293 K): δ 1.85 (br, 4 H, $H_{ethylene}$), 3.15 (br, 4 H, $H_{ethylene}$), 6.07 (t, 2 H, $H_{m,\eta^6\text{-}Ph}$, $^3J_{H_m-H_o} = {}^3J_{H_m-H_p} \cong 6.38$ Hz), 6.44 (d, 2 H, $H_{o,\eta^6\text{-}Ph}$), 6.98 (m, 1 H, $H_{p,\eta^6\text{-}Ph}$), 7.02 (m, 3 H, H_{p,BPh_3}), 7.14 (m, 6 H, H_{m,BPh_3}), 7.32 (d, 6 H, H_{o,BPh_3}, $^3J_{H_o-H_m} = 7.22$ Hz). ^{13}C NMR (THF-d_8, 293 K): δ 50.28 (d, $C_{ethylene}$, $J_{C-Rh} = 12.7$ Hz); 103.37 (d, $J_{C-Rh} = 1.8$ Hz), 104.40 (d, $J_{C-Rh} < 1.5$ Hz), and 110.09 (d, $J_{C-Rh} = 2.7$ Hz), $C_{o,m,p}$ of the coordinated phenyl ring;[54] 123.75, 126.52, and 136.83, $C_{o,m,p}$ of the uncoordinated phenyl rings; 158.7 (C_{ipso,BPh_3}).[55]

Synthesis of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3$ (3). Silver triflate (0.1983 g, 0.771 mmol) in THF (5 mL) was added, under an ethylene stream, to a filtered, cold (253 K) solution of $[Rh(C_2H_4)_2Cl]_2$[53] (0.1670 g, 0.429 mmol) in THF (20 mL). After stirring for 30 min, the reaction mixture was filtered. The mother and washing solutions, collected together, were slowly added, under a dinitrogen stream, to a cooled (273 K) solution of **1** (0.3638 g, 0.770 mmol) in THF (120 mL). The resulting solution was stirred at 273 K for 3 h, then concentrated in vacuo to a small volume, and cooled to 253 K. $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot 0.5THF$ separated as a yellow microcrystalline solid which was filtered out, washed with n-pentane, and dried in vacuo (m = 0.510 g, 0.62 mmol, 81% vs AgO_3SCF_3). The IR spectrum of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot 0.5THF$ shows features analogous to those of **3** (see below). The ^1H NMR spectrum of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot 0.5THF$ is identical with that of **3** except for the presence of two multiplets at 3.67 and 1.81 ppm due to the crystallization THF. Anal. Calcd for $C_{35}H_{40}BF_3O_{3.5}Rh_2S$: C, 51.12; H, 4.90. Found: C, 50.96; H, 5.03. $\Lambda_M(PhNO_2, 4.46 \times 10^{-3}\ M) = 22.3\ S\ cm^2\ mol^{-1}$.[56]

Recrystallization of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot 0.5THF$ from CH_2Cl_2/n-pentane gives quantitatively pure **3**. Anal. Calcd for $C_{33}H_{36}BF_3O_3Rh_2S$: C, 50.41; H, 4.61. Found: C, 50.36; H, 4.62. IR (Nujol, KBr disks, cm^{-1}): 1428 (m-s), 1395 (m-s), 1275 (vs), 1223 (m-s), 1170 (s), 1030 (s, sh), 823 (w), 805 (m), 630 (s, sh), 571 (m), 517 (m). ^1H NMR (CD_2Cl_2, 293 K): δ 2.07 (br, 8 H, $H_{ethylene}$), 3.27 (br, 8 H, $H_{ethylene}$), 6.36 (t, 4 H, $H_{m,\eta^6\text{-}(Ph)_2}$, $^3J_{H_m-H_o} \cong {}^3J_{H_m-H_p} = 6.38$ Hz), 6.52 (d, 4 H, $H_{o,\eta^6\text{-}(Ph)_2}$), 7.13 (m, 2 H, H_{p,BPh_2}), 7.24 (m, H_{m,BPh_2}), 7.26 (t, $H_{p,\eta^6\text{-}(Ph)_2}$), 7.40 (d, 4 H, H_{o,BPh_2}, $^3J_{H_o-H_m} = 6.84$ Hz). ^{13}C NMR ($CDCl_3$, 293 K): δ 51.19 (d, $C_{ethylene}$, $J_{C-Rh} = 12.1$ Hz); 103.09 (d, $J_{C-Rh} = 2.5$ Hz), 104.88 (d, $J_{C-Rh} \approx 1$ Hz), and 108.67 (d, $J_{C-Rh} = 3.4$ Hz), $C_{o,m,p}$ of the coordinated phenyl rings; 125.07, 126.93, and 135.60, $C_{o,m,p}$ of the uncoordinated phenyl rings.

Reaction of 2 with (diphos)$Rh(\eta^6\text{-}PhBPh_3)$. A THF solution of **2**, prepared as reported above {0.1897 g, 0.487 mmol of $[Rh(C_2H_4)_2Cl]_2$; 0.2253 g, 0.877 mmol of AgO_3SCF_3}, was added to a cooled (253 K) solution of (diphos)$Rh(\eta^6\text{-}PhBPh_3)$ (0.7195 g, 0.877 mmol) in THF (100 mL), and the mixture was stirred overnight at that temperature. The solution was, then, concentrated in vacuo and cooled to 243 K to yield a yellow precipitate, $(C_2H_4)_2Rh(\eta^6\text{-}PhBPh_3)\cdot THF$, that was filtered out, washed with cold THF/n-pentane (1:3 v/v), and dried in vacuo [m = 0.102 g, 0.18 mmol, 21% vs (diphos)$Rh(\eta^6\text{-}PhBPh_3)$]. Some more pure compound could be obtained from the mother solution by fractionated crystallization using n-pentane (overall yield: 0.194 g, 0.35 mmol, 40%). Anal. Calcd for $C_{32}H_{36}BORh$: C, 69.85; H, 6.58. Found: C, 69.58; H, 6.72. IR (Nujol, KBr disks): see ref 50.

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(53) About 10% of the weighted mass was insoluble in the reaction solvent (toluene).

(54) In CD_2Cl_2 (293 K) these carbon atoms resonate at 104.29 (d, J_{C-Rh} = 2.9 Hz), 105.09 (d, J_{C-Rh} = 2.5 Hz), and 111.01 ppm (d, J_{C-Rh} = 2.4 Hz). The signal due to the ethylene ligands is a doublet at 52.00 ppm (J_{C-Rh} = 12.0 Hz).

(55) The assignment of this signal has been made on the analogy of the other data reported in the literature.[10,12,13,21]

(56) $\Lambda_M(PhNO_2, 10^{-3}\ M)$ ranges around 22–25 S cm^2 mol^{-1} for 1:1 electrolytes.[57]

(57) (a) Cannon, R. D.; Chiswell, B.; Venanzi, L. M. *J. Chem. Soc. A* **1967**, 1277. (b) Halfpenny, M. T.; Hartley, J. G.; Venanzi, L. M. *J. Chem. Soc. A* **1967**, 627.

Table IV. Experimental Data for the X-Ray Diffraction Study of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot(CH_3)_2CO$ [3·(CH$_3$)$_2$CO]

formula	$C_{36}H_{42}BF_3O_4Rh_2S$
mol wt	844.402
cryst dimens, mm	0.30 × 0.28 × 0.42
data coll T, K	296
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	13.050(1)
b, Å	14.805(2)
c, Å	19.736(4)
β, deg	70.71(1)
V, Å^3	3587.5
Z	4
ρ(calcd), g cm^{-3}	1.577
μ, cm^{-1}	10.095
radiation (λ, Å)	graphite-monochromated Mo Kα (0.710 69)
measd reflns	$\pm h,+k,+l$
θ range, deg	$2.60 < \theta < 25.0$
scan type	$\omega/2\theta$
scan width, deg	$1.10 + 0.35 \tan\theta$
max counting time, s	70
bkgd time, s	0.5 × scan time
max scan speed, deg min^{-1}	10.5
prescan rejection limit	0.55 (1.82σ)
prescan acceptance limit	0.025 (40.00σ)
horiz receiving slit, mm	$1.70 + \tan\theta$
vert receiving slit, mm	4.0
no. ind data coll	5976
no. obs reflns (n_o) ($\|F_o\|^2 > 3.0\sigma(\|F\|)^2$)	3358
transm coeff	0.8322–0.9985
decay correct factors	0.9953–2.7279
no. of params refined (n_v)	424
R^a	0.058
$R_w{}^b$	0.080
GOF^a	2.018

[a] $R = \sum(\|F_o\| - (1/k)\|F_c\|)/\sum\|F_o\|$. [b] $R_w = [\sum w(\|F_o\| - (1/k)\|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$ where $w = [\sigma^2(F_o)]^{-1}$ and $\sigma(F_o) = [\sigma^2(F_o{}^2) + f^4(F_o{}^2)]^{1/2}/2F_o$ with $f = 0.045$. [c] $\mathrm{GOF} = [\sum w(\|F_o\| - (1/k)\|F_c\|)^2/(n_o - n_v)]^{1/2}$.

Synthesis of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_3BPh\}(O_3SCF_3)_2$ (4). A THF solution (30 mL) of **2**, prepared in situ (see above) under ethylene from silver triflate (0.5270 g, 2.05 mmol) and $[Rh(C_2H_4)_2Cl]_2$ (0.3590 g, 0.924 mmol), was slowly added, under a dinitrogen stream, to a cooled (273 K) solution of **1** (0.4410 g, 0.924 mmol) in THF (120 mL). The resulting solution was stirred at 273 K for 5 h and, then, concentrated in vacuo. The yellow solid precipitated was filtered out, washed with cold THF and *n*-pentane, and dried in vacuo. More compound could be obtained from the mother solution by addition of pentane and cooling to 253 K (0.808 g, 0.74 mmol, 80% overall yield vs **1**). Anal. Calcd for $C_{38}H_{44}BF_6O_6Rh_3S_2$: C, 41.71; H, 4.05. Found: C, 41.55; H, 4.01. IR (Nujol, KBr disks, cm^{-1}): 1392 (m-s), 1276 (vs), 1223 (s), 1161 (s), 1029 (m), 810 (m), 638 (s), 572 (m), 517 (m). ^{1}H NMR (CD_2Cl_2, 293 K): δ 2.20 (br, 12 H, $H_{ethylene}$), 3.25 (br, 12 H, $H_{ethylene}$), 6.56 (t, 6 H, $H_{m,\eta^6\text{-}(Ph)_3}$, $^3J_{H_m-H_o} \cong {}^3J_{H_m-H_p} = 5.9$ Hz), 6.69 (d, 6 H, $H_{o,\eta^6\text{-}(Ph)_3}$), 7.34 (m, $H_{m,BPh}$), 7.39 (m, $H_{p,\eta^6\text{-}(Ph)_3}$), 7.40 (m, $H_{m,BPh}$), 7.69 (d, 2 H, $H_{o,BPh}$, $^3J_{H_o-H_m} = 7.16$ Hz).

Crystallography. Yellow crystals of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot(CH_3)_2CO$, suitable for X-ray structural analysis, were obtained by crystallization of $\{[(C_2H_4)_2Rh(\eta^6\text{-}Ph)]_2BPh_2\}O_3SCF_3\cdot0.5THF$ from anhydrous acetone and are fragile and stable in air only for short periods of time, possibly due to the loss of solvent. A prismatic crystal was chosen for the data collection, covered by acrylic resin for protection, and mounted on a glass fiber at a random orientation.

An Enraf-Nonius CAD4 diffractometer was used both for the unit cell and space group determination and for the data collection. Unit cell dimensions were obtained by least squares fit of the 2θ values of 25 high-order reflections ($9.0° < \theta < 16.3°$) using the CAD4 centering routines. Selected crystallographic and other experimental data are listed in Table IV.

Table V. Final Positional Parameters and Equivalent Temperature Factors for [3·(CH$_3$)$_2$CO] (Esd's Given in Parentheses)

atom	*x*	*y*	*z*	*B*,^{a} Å^2
Rh1	0.30893(7)	0.12193(6)	0.04784(6)	3.49(2)
Rh2	0.03631(9)	0.39897(6)	0.17129(6)	4.16(2)
S	–0.3216(5)	0.3112(5)	–0.1299(4)	12.3(2)
F1	–0.185(1)	0.193(1)	–0.188(1)	20.1(8)
F2	–0.137(1)	0.274(1)	–0.123(1)	18.9(7)
F3	–0.130(2)	0.313(1)	–0.220(1)	23(1)
O1	–0.381(1)	0.303(1)	–0.177(1)	14.8(6)
O2	–0.342(2)	0.210(1)	–0.093(1)	20.2(9)
O3	–0.336(2)	0.386(1)	–0.116(2)	27(1)
CF	–0.196(2)	0.268(1)	–0.166(1)	10.7(7)
C1	0.1215(8)	0.1439(7)	0.0673(7)	3.0(3)
C2	0.1617(8)	0.0624(8)	0.0285(7)	3.5(3)
C3	0.2103(9)	–0.0102(8)	0.0617(8)	4.4(3)
C4	0.2291(9)	0.0051(8)	0.1263(7)	4.1(3)
C5	0.199(1)	0.0897(9)	0.1607(8)	4.4(3)
C6	0.1412(9)	0.1566(8)	0.1323(7)	3.7(3)
C7	0.0543(9)	0.3164(8)	0.0635(7)	3.4(3)
C8	0.151(1)	0.3574(9)	0.0596(7)	4.2(3)
C9	0.161(1)	0.452(1)	0.0746(8)	6.0(4)
C10	0.070(1)	0.510(1)	0.0834(9)	6.4(5)
C11	–0.033(1)	0.4730(9)	0.0940(8)	5.6(4)
C12	–0.038(1)	0.3772(8)	0.0851(8)	4.5(3)
C13	0.0744(9)	0.2127(8)	–0.0471(7)	3.5(3)
C14	0.047(1)	0.1392(9)	–0.0835(8)	4.8(4)
C15	0.068(1)	0.138(1)	–0.1561(9)	6.4(5)
C16	0.124(1)	0.208(1)	–0.1985(9)	6.3(5)
C17	0.154(1)	0.283(1)	–0.1635(9)	6.1(4)
C18	0.130(1)	0.2836(9)	–0.0909(8)	4.7(4)
C19	–0.0833(9)	0.1782(8)	0.0778(7)	3.4(3)
C20	–0.1645(9)	0.2088(9)	0.0540(8)	4.6(4)
C21	–0.273(1)	0.184(1)	0.0845(8)	5.2(4)
C22	–0.301(1)	0.126(1)	0.1375(9)	6.3(4)
C23	–0.222(1)	0.089(1)	0.1690(9)	6.3(4)
C24	–0.113(1)	0.1156(8)	0.1341(8)	4.3(3)
C111	0.367(1)	0.180(1)	–0.0581(8)	5.2(4)
C112	–0.120(1)	0.388(1)	0.2583(9)	6.1(4)
C121	0.405(1)	0.220(1)	0.0804(9)	6.3(4)
C122	0.093(1)	0.466(1)	0.2485(8)	7.7(4)
C211	0.415(1)	0.094(1)	–0.0592(8)	5.8(4)
C212	–0.065(1)	0.3036(9)	0.2450(8)	5.3(4)
C221	0.453(1)	0.133(1)	0.0768(9)	6.9(4)
C222	0.150(1)	0.390(1)	0.2310(8)	6.7(4)
B	0.042(1)	0.2121(9)	0.0408(8)	3.2(3)
OS1^b	–0.293(2)	0.466(2)	0.136(1)	21(1)
CS1	–0.381(2)	0.484(2)	0.133(2)	13.8(9)
CS2	–0.466(3)	0.420(3)	0.134(2)	26(2)
CS3	–0.429(3)	0.555(2)	0.187(2)	21(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. [b] The atoms labeled CS and OS belong to the clathrated solvent molecule.

Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and measured every hour. The orientation of the crystal was checked by measuring three other reflections every 300 measurements. Data have been corrected for Lorentz and polarization factors and for decay using the data reduction programs of the SDP crystallographic package.[58] An empirical absorption correction[59] was applied by using azimuthal (Ψ) scans of three "high-χ-angle" reflections ($\chi > 86°$; $8° < \theta < 17°$).

The standard deviations on intensities were calculated in terms of statistics alone, while those on F_o were calculated as reported in Table IV.

Intensities were considered as observed if $\|F_o{}^2\| > 3.0\sigma(F^2)$ and used for the solution and refinement of the structure. A $F_o = 0.0$

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(58) *SDP Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, The Netherlands, 1989.

(59) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351.

was given to those reflections having negative net intensities.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares.[59] The function minimized was $[\sum w(|F_o| - 1/k|F_c|)^2]$. No extinction correction was applied.

The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[60] Anisotropic temperature factors were used for all atoms.

Toward the end of the refinement a solvent molecule, $(CH_3)_2CO$, was located in a Fourier difference map and included in the refinement. Both the triflate counterion and the acetone molecule are highly disordered, as shown by the high thermal factors, and only an approximate geometry has been obtained from the refinement. The contribution of the hydrogen atoms in their idealized positions (C–H = 0.95 Å, $B = 8.0$ Å^2) was taken into account but not refined.

Upon convergence no parameter shift was $>0.4\sigma(p)$. All calculations were carried out by using the Enraf-Nonius SDP crystallographic programs.[58]

The final atomic coordinates and equivalent thermal factors are given in Table V.

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Supplementary Material Available: Tables of anisotropic temperature factors (Table S1), bond distances (Table S2) and angles (Table S3), and torsion angles (Table S4) (10 pages). Ordering information is given on any current masthead page.

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(60) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.