# Reaction Patterns of Hydrido(phosphine)rhodium(I) Compounds with Electrophilic Olefins and Molecular Structure of a Product Formed from *trans*-$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$ and Dimethyl Fumarate

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## Abstract

While a reaction of $RhH[P(i\text{-}Pr)_3]_3$ with dimethyl fumarate (DF) afforded *trans*-$RhH(DF)[P(i\text{-}Pr)_3]_2$ (1), a similar reaction of *trans*-$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$ with DF took place through dissociation of one phosphine ligand and C-metallation of a tert-butyl group to give $Rh[CH_2CMe_2PPh(t\text{-}Bu)](DF)_2$ (2). These compounds were characterized by $^1H$ and $^{13}C$ NMR spectra and the molecular structure of 2 was elucidated by an X-ray study. Crystals of 2 are monoclinic, space group $C2/c$ with $a$ = 35.531(5), $b$ = 9.499(1), $c$ = 38.851(5) Å, $\beta$ = 120.362(9)°, and $Z$ = 16. The weighted and unweighted $R$ values were 0.063 and 0.091, respectively (for 5488 reflections). The Rh atom assumes a highly distorted trigonal bipyramidal configuration with the P atom and two DF molecules in the equatorial plane, and the methylene carbon and a methoxy oxygen atom of an ester group at the axial sites. The reaction patterns leading to the observed products rather than to the olefin insertion products are discussed.

## Introduction

Rhodium(I) hydrido compounds $RhHL_n$ (L = $P(i\text{-}Pr)_3$, $PPh(t\text{-}Bu)_2$, *etc.*; n = 2, 3) [1–3] are perhaps one of the most versatile Group 8 transition metal compounds having tert-phosphines. They serve as efficient catalysts for the water gas shift reaction [4, 5] and hydrogenation of alkynes [6], ketones [7], or nitriles [8] through their capability of activating $H_2O$ [9, 10] and $H_2$ [1], respectively. Their exceedingly high reactivity is apparently due to their propensity to form coordinatively-unsaturated species in solution. We expected facile reactions between $RhHL_2$ and somewhat larger electrophiles such as alkynes or activated olefins from our experience with the $PtL_2$ chemistry [11]. Thus we investigated the reaction with a good electron-accepting olefin, dimethyl fumarate (DF), in expectation of obtaining a σ-alkyl compound, $Rh(R)L_2$. The reaction of DF with $RhH[P(i\text{-}Pr)_3]_3$ gave a simple adduct, *trans*-$RhH(DF)[P(i\text{-}Pr)_3]_2$, which could be readily identified by spectroscopic means, as will be described below. The reaction with *trans*-$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$, however, underwent a different reaction producing a compound whose elemental analysis indicated a composition close to $RhH(DF)_2[PPh(t\text{-}Bu)_2]$ or $Rh[CH(CO_2Me)CH_2\text{-}CO_2Me](DF)[PPh(t\text{-}Bu)_2]$. Although the possibility of the former was readily excluded by $^1H$ NMR spectrum through the absence of a metal hydrido proton, conclusive evidence as to the latter, a σ-alkyl olefin complex, could not be obtained from the spectroscopic data. An X-ray study revealed a unique molecular structure involving C-metallation of the $PPh(t\text{-}Bu)_2$ and a bidentate coordination of one of the DF molecules through the C=C bond and a methoxy oxygen atom of the ester group. We therefore wish to describe details of the interesting molecular structure together with some preparative aspects. That the reaction of DF with both $RhH[P(i\text{-}Pr)_3]_3$ and *trans*-$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$ does not give an olefin insertion product is rather unexpected, and this will also be discussed.

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## Experimental

All reactions and manipulations were carried out under dinitrogen atmosphere. $^1$H and $^{13}$C NMR spectra were measured on a JEOL JNM-4H-100 or a Brucker WH-400, and IR spectra on a Hitachi Perkin-Elmer Model 295 spectrometer. RhH[P(i-Pr)$_3$]$_3$ [1] and *trans*-RhH(N$_2$)[PPh(t-Bu)$_2$]$_2$ [3] were prepared by the methods previously reported.

*trans-RhH(DF)[P(i-Pr)$_3$]$_2$ (1)*

A mixture of RhH[P(i-Pr)$_3$]$_3$ (0.12 g, 0.2 mmol) and DF (0.06 g, 0.45 mmol) in toluene (5 ml) was stirred for 0.5 h at room temperature. After concentration of the red solution to a quarter of the original volume, the concentrate was kept at −30° to give red crystals (0.1 g, 88%), mp 130 °C dec. *Anal.* Calcd for $C_{24}H_{51}O_4P_2Rh$: C, 50.71; H, 9.04. Found: C, 50.41; H, 8.87.

*Rh[CH$_2$CMe$_2$PPh(t-Bu)](DF)$_2$ (2)*

To a solution of *trans*-RhH(N$_2$)[PPh(t-Bu)$_2$]$_2$ (0.17 g, 0.3 mmol) in toluene (10 ml) was added DF (0.10 g, 0.7 mmol) at room temperature. Immediately the yellow solution turned pale red. The mixture was concentrated and solid residue was recrystallized twice from n-hexane–toluene to give a yellow crystal (0.13 g, 72%), mp 120 °C dec. *Anal.* Calcd for $C_{26}H_{38}O_8PRh$: C, 50.98; H, 6.21. Fround: C, 51.05; h, 6.28. A similar reaction of dimethyl maleate with *trans*-RhH(N$_2$)[PPh(t-Bu)$_2$]$_2$ gave **2** in 50% yield.

*An X-ray Study of Rh[CH$_2$CMe$_2$PPh(t-Bu)](DF)$_2$ (2)*

Crystals suitable for an X-ray analysis were grown from a toluene–n-hexane solution. A tabular specimen, approximately 0.36 × 0.24 × 0.15 mm, was sealed in an argon-filled capillary tube to prevent decomposition. Preliminary photographic data showed that the crystal was monoclinic of space group $C2/c$ or $Cc$. The space group $C2/c$ was confirmed by a successful analysis. The unit cell dimensions were determined with MoK$\alpha$ radiation ($\lambda$ = 0.71069 Å) by a least-squares fit of 48 reflections in the range 20° < 2$\theta$ < 26° measured on a Rigaku four-circle automatic diffractometer. *Crystal data*: $a$ = 35.531(5), $b$ = 9.499(1), $c$ = 38.851(5) Å, $\beta$ = 120.362(9)°, $V$ = 11314(2) Å$^3$, $Z$ = 16, $D_x$ = 1.4383(3) g cm$^{-3}$.

Intensities for the independent reflections for 2$\theta$ less than 50° were measured with the $\omega$–2$\theta$ continuous scan mode at a 2$\theta$ rate of 4° min$^{-1}$, by use of MoK$\alpha$ radiation monochromated with a graphite crystal. The scan width in $\omega$ was (0.9 + 0.34 tan$\theta$)° with stationary background counts of 15 s duration on either side of the peak. As a check of the deterioration of the specimen the intensities of 5 reflections were measured before every 50 reflections. No notable variations were observed for the intensities during the data collection. The intensities were corrected for Lorentz and polarization factors, but not for absorption ($\mu$ = 6.92 cm$^{-1}$ for MoK$\alpha$). Of 10,114 reflections measured, 4565 reflections with $|F_0| < 3\sigma(F)$ and 61 reflections, which were influenced apparently by the neighboring reflections, were excluded; thus 5488 reflections were considered observed and used for structure determination.

The space group $C2/c$ assumed and the value of $Z$ suggest that the unit cell contains two crystallographically-independent molecules, I and II. The structure was solved by the usual heavy atom method. The rhodium and phosphorus atoms were located from a Patterson map. An iterative application of Fourier and diagonal least-squares calculations gave a reasonable set of coordinates and isotropic thermal factors of all non-hydrogen atoms. At this stage the residual index, $R = \Sigma|\Delta F|/\Sigma|F_0|$, was 0.11 where $\Delta F = |F_0| - |F_c|$. In the least-squares calculations the function minimized was $\Sigma w(\Delta F)^2$, where $w$ was the weight. The subsequent block-diagonal least-squares refinements involving anisotropic thermal parameters converged to $R$ of 0.091 and $R_w = [\Sigma w|F|^2/\Sigma w|F_0|^2]^{1/2}$ of 0.063. In the final refinement cycle the weighting scheme, $1/w = \sigma^2(F_0) + 0.00001|F_0|^2$, was used. A difference Fourier map calculated at this stage showed many peaks, probably due to the hydrogen atoms. However, attempts to find all hydrogen atoms were unsuccessful and they were not included in the refinement.

Atomic scattering factors were taken from the usual tabulation [12]. The anomalous dispersion correction [13] for the rhodium and phosphorus atoms were included in the structure factor calculations. The final atomic coordinates are listed in Table I. Tables of temperature and structure factors are available as supplementary material**.

## Results and Discussion

*Preparation of trans-RhH(DF)[P(i-Pr)$_3$]$_2$ (1) and Rh[CH$_2$CMe$_2$PPh(t-Bu)](DF)$_2$ (2) (DF = dimethyl fumarate) and Their Characterization*

Reaction of RhH[P(i-Pr)$_3$]$_3$ with two mol of DF in toluene occurs readily at room temperature, to give quantitatively a hydrido olefin bis-phosphine complex *trans*-RhH(DF)[P(i-Pr)$_3$]$_2$ (**1**) as orange crystals. Interestingly, a $\sigma$-alkyl compound such as [Rh[CH(CO$_2$Me)CH$_2$CO$_2$Me](DF)[P(i-Pr)$_3$]$_2$ was

**All computations were carried out on FACOM 230/38 and HITAC M-160H computers of Information Processing Research Center, Kwansei Gakuin University, and a MELCOM 70/30 of our laboratory.

TABLE I. Final Atomic Coordinates ($\times 10^4$)[a] for Molecules I and II of **2**.

| Molecule I | | | | Molecule II | | | |
|---|---|---|---|---|---|---|---|
| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
| Rh(1) | 3864.6(4) | 3845(1) | 1385.4(3) | Rh(2) | 1298.6(3) | 2524(1) | 1226.3(3) |
| P(1) | 3779(1) | 6191(4) | 1536(1) | P(2) | 1065(1) | 143(4) | 1088(1) |
| C(1) | 4178(4) | 6655(14) | 1358(4) | C(27) | 1543(4) | −255(15) | 1626(4) |
| C(2) | 4327(4) | 5151(13) | 1366(4) | C(28) | 1598(5) | 1338(15) | 1762(4) |
| C(3) | 3243(4) | 7016(14) | 1243(4) | C(29) | 1122(4) | −851(13) | 713(4) |
| C(4) | 2893(4) | 6193(18) | 1189(4) | C(30) | 1003(4) | −152(17) | 353(4) |
| C(5) | 2470(5) | 6818(19) | 994(5) | C(31) | 1014(5) | −907(17) | 44(4) |
| C(6) | 2387(5) | 8209(18) | 865(5) | C(32) | 1145(5) | −2296(18) | 99(4) |
| C(7) | 2755(5) | 9027(17) | 909(4) | C(33) | 1284(5) | −2983(16) | 475(5) |
| C(8) | 3178(5) | 8396(15) | 1088(4) | C(34) | 1259(4) | −2267(15) | 777(4) |
| C(9) | 3958(5) | 6943(15) | 2054(4) | C(35) | 513(5) | −538(17) | 999(6) |
| C(10) | 3980(5) | 8556(14) | 2061(5) | C(36) | 504(5) | −2145(16) | 1010(4) |
| C(11) | 3605(6) | 6428(18) | 2152(5) | C(37) | 180(4) | −88(21) | 576(6) |
| C(12) | 4399(5) | 6331(20) | 2377(4) | C(38) | 402(5) | 110(20) | 1293(6) |
| C(13) | 3919(5) | 7195(15) | 917(4) | C(39) | 1934(4) | −780(16) | 1604(4) |
| C(14) | 4549(4) | 7655(17) | 1594(4) | C(40) | 1467(5) | −1161(18) | 1895(4) |
| C(15) | 2336(4) | 5191(21) | 126(5) | C(41) | 1834(5) | 1357(17) | 234(4) |
| C(16) | 2999(4) | 3996(17) | 571(4) | C(42) | 1765(4) | 2441(16) | 747(4) |
| C(17) | 3482(4) | 3956(15) | 742(4) | C(43) | 1880(4) | 2391(16) | 1168(4) |
| C(18) | 3686(4) | 2628(17) | 869(4) | C(44) | 1851(4) | 3717(16) | 1320(3) |
| C(19) | 4032(4) | 2257(14) | 780(4) | C(45) | 2188(4) | 4099(16) | 1736(4) |
| C(20) | 4471(5) | 335(17) | 755(5) | C(46) | 2577(5) | 5966(18) | 2200(4) |
| C(21) | 3010(4) | 2124(19) | 1553(4) | C(47) | 551(5) | 4061(19) | 187(4) |
| C(22) | 3765(4) | 2657(17) | 1975(4) | C(48) | 475(5) | 3717(18) | 778(5) |
| C(23) | 4178(4) | 3024(15) | 1984(4) | C(49) | 725(4) | 3426(15) | 1210(4) |
| C(24) | 4293(4) | 2167(15) | 1753(4) | C(50) | 1104(4) | 4319(15) | 1450(4) |
| C(25) | 4760(4) | 2202(15) | 1869(4) | C(51) | 1269(4) | 4281(14) | 1891(4) |
| C(26) | 5350(5) | 997(22) | 1871(5) | C(52) | 1771(5) | 5289(19) | 2507(4) |
| O(1) | 2808(3) | 5079(11) | 338(3) | O(9) | 1924(3) | 1340(10) | 648(2) |
| O(2) | 4132(3) | 836(9) | 843(3) | O(10) | 2235(3) | 5521(10) | 1805(3) |
| O(3) | 2786(3) | 3113(12) | 629(3) | O(11) | 1553(3) | 3372(11) | 502(3) |
| O(4) | 4225(3) | 3024(10) | 678(3) | O(12) | 2417(3) | 3291(10) | 2008(3) |
| O(5) | 3452(3) | 2300(11) | 1612(3) | O(13) | 749(3) | 3962(11) | 630(3) |
| O(6) | 4880(3) | 1114(12) | 1739(3) | O(14) | 1594(3) | 5236(11) | 2084(3) |
| O(7) | 3712(3) | 2770(12) | 2258(3) | O(15) | 83(3) | 3635(14) | 564(3) |
| O(8) | 5011(3) | 3164(11) | 2053(3) | O(16) | 1121(3) | 3551(11) | 2043(3) |

[a]E.s.d.s are in parentheses.

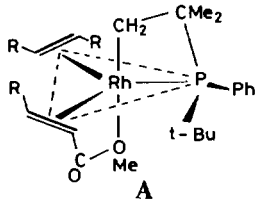
not formed. The IR spectrum (nujol mull) showed $\nu$(Rh–H) and $\nu$(C=O) at 1980 and 1680 $cm^{-1}$, respectively. A *trans* square planar structure is readily inferred from the hydrido signal observed at $\delta$ −8.8 as a double triplet ($J_{H-P}$ = 5.2 Hz, $J_{H-Rh}$ = 20.5 Hz) in the $^1H$ NMR spectrum measured in benzene-$d_6$. The olefinic proton signal also appears as double triplet at $\delta$ 4.10 ($J_{H-P}$ = 3.1 Hz, $J_{H-Rh}$ = 1.6 Hz) together with the $CH_3O$ signal at $\delta$ 3.53(s). Observation of two methyl proton signals due to the diastereotopic methyl groups of P(i-Pr)$_3$ at $\delta$ 1.16 and 1.20 in equal intensity and with the same coupling constants ($^3J_{H-P} + {}^5J_{H-P}$ = 13.6 Hz, $J_{H-H}$ = 5.8 Hz) is consistent with both perpendicular and parallel coordinations of the olefin with respect to the molecular plane. The geometry of a coordinated olefin in $d^8$ square planar complexes has been suggested to be determined largely by steric factors rather than electronic ones [14]. In view of the steric bulk of P(i-Pr)$_3$ (cone angle 160° [15]), it is reasonable to assume that the DF molecule in **1** coordinates perpendicularly.

The reaction of a Rh(I) hydride carrying the more bulky PPh(t-Bu)$_2$ ligand (cone angle 170° [16]) *trans*-RhH(N$_2$)[PPh(t-Bu)$_2$]$_2$ with two mol of DF proceeds through dissociation of one mol of the phosphine and C-metallation of a tert-butyl group. A $\sigma$-alkyl monophosphine bis-olefin complex Rh[CH$_2$CMe$_2$PPh(t-Bu)](DF)$_2$ (**2**) was obtained as yellow crystals in a reasonable yield. The compound **2** was also obtainable from the reaction of the corresponding *cis*-olefin, indicating a facile, incipient *cis–trans* isomerization. Dissociation of one PPh(t-Bu)$_2$ ligand from *trans*-RhH(N$_2$)[PPh(t-Bu$_2$]$_2$

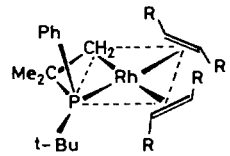
is expected since a similar reaction of isoelectronic $M[PPh(t\text{-}Bu)_2]_2$ (M = Pd, Pt) with DF gave $M(DF)_2[PPh(t\text{-}Bu)_2]$ [11].

The presence of the phosphorus atom containing a four-membered chelate ring was readily deduced from the 400 MHz $^1H$ and 100 MHz $^{13}C$ NMR spectra (Table II). Thus, two $\sigma$-$CH_2$ proton signals and two $CH_3$ proton and $^{13}C$ signals were observed. The non-equivalence of the respective signals is induced by the asymmetrical substituents of PPh(t-Bu) group involved in the four-membered chelate ring. In addition, the different magnitude of $J_{H-P}$ of the $CH_2$ protons indicates the non-planarity of the chelate ring, which was confirmed by the present X-ray structural analysis (*vide infra*). The observation of four different proton and $^{13}C$ signals of the olefinic groups, as well as four different $CH_3O$ proton and $^{13}C$ signals of the ester groups, indicates a rigid coordination of two DF molecules in different chemical environments. Based on the magnitude of *trans* olefinic proton couplings, a pair of the higher field olefinic proton signals is assignable to one DF molecule, while those observed at the lower field are due to the other molecule (Table II). A square planar structure **B** and **C** may be conceivable either with parallel or perpendicular coordination of two DF molecules with respect to the molecular plane. In those two structures the magnitudes of $J_{H-P}$ and $J_{C-P}$ of the olefin *trans* to the phosphorus atom are expected to be larger than those of *cis*. The magnitudes of a pair of $J_{H-P}$ of each olefin and also that of $J_{C-P}$ were found to be similar. In fact, **2** was proved to assume a trigonal bipyramidal structure (A) rather than the square planar alternatives **B** and **C** by the present X-ray structural study.

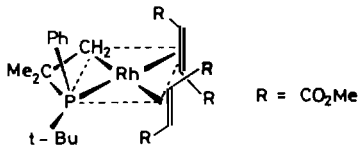
The preferential C-metallation of the tert-butyl group in $PPh_n(t\text{-}Bu)_{3-n}$ (n = 1, 2) ligand has pre-




A




B




C

cedents, $[Pd\overline{CH_2CMe_2}PPh(t\text{-}Bu)(\mu\text{-}Cl)]_2$ [17] and $Ru\overline{H(CH_2CMe_2}PPh_2)(\eta^6\text{-}C_6Me_6)$ [18]. These aliphatic carbon metallations are in contrast to the selective aromatic metallation in the formation of $Pt[C_6H_4P(t\text{-}Bu)_2](Cl)PPh(t\text{-}Bu)_2$ from *trans*-$PtCl_2[PPh(t\text{-}Bu)_2]_2$ [19].

*Structure of $Rh\overline{[CH_2CMe_2}PPh(t\text{-}Bu)](DF)_2$ (2)*

The crystal structure of **2** shown in stereoview (Fig. 1) contains two discrete and crystallographically independent molecules, separated by van der Waals distances. The selected interatomic distances and bond angles are given in Table III. The molecular structures of two independent molecules I and II are shown in Figs. 2 and 3 respectively. Since the molecular geometries of these two molecules differ only slightly (Table III), description and discussion will be made mainly on the molecule I. Assuming the olefin to be a unidentate ligand, the coordination geometry around the Rh(1) atom in the molecule I can be regarded as being a highly distorted trigonal bipyramid with the P(1) atom and two DF molecules in the equatorial plane and

TABLE II. $^1H$ and $^{13}C$ NMR Spectral Data of $Rh\overline{[CH_2CMe_2}PPh(t\text{-}Bu)](DF)_2$[a,b].

| | $^1H$ NMR[c] | | | | | $^{13}C$ NMR[c,d] | | |
|---|---|---|---|---|---|---|---|---|
| | $\delta$ | $J_{H-P}$ (Hz) | $J_{H-H}$ (Hz) | $J_{H-Rh}$ (Hz) | | $\delta$ | $J_{C-P}$ (Hz) | $J_{C-Rh}$ (Hz) |
| $RhCH_2$ | 0.85(q) | 2.7 | 5.4 | 2.7 | $RhCH_2$ | 25.64(dd) | 24.0 | 29.0 |
| | 1.50(dt) | 20.3 | 5.4 | 2.7 | | | | |
| $Me_2C$ | 0.94(d) | 13.5 | | | *Me*$_2$C | 28.50(s) | | |
| | 1.42(d) | 12.9 | | | | 30.58(s) | | |
| | | | | | Me$_2$*C* | 36.46(d) | 7.6 | |
| $Me_3C$ | 1.12(d) | 13.0 | | | *Me*$_3$C | 29.50(d) | 4.4 | |
| | | | | | Me$_3$*C* | 51.93(d) | 18.3 | |
| CH= | 4.20(dt) | 2.0 | 10.5 | 2.0 | *C*H= | 56.30(t) | 9.2 | 9.2 |
| | 4.36(o) | 1.2 | 10.5 | 6.4 | | 57.06(dd) | 4.6 | 12.2 |
| | 5.02(o) | 2.2 | 8.8 | 4.6 | | 58.14(dd) | 10.7 | 15.3 |
| | 5.62(dd) | 0 | 8.8 | 7.8 | | 62.71(dd) | 4.6 | 9.2 |

[a]Measured in toluene-$d_8$ at −15 °C. [b]DF = *trans*-$MeO_2CCH{=}CHCO_2Me$. [c]MeO signals ($\delta$), $^1H$ NMR: 2.90(s), 3.22(s), 3.32(s), 3.58(s); $^{13}C$ NMR: 50.61(s), 50.85(s), 51.34(s), 51.46(s). [d]$^{13}C$ NMR($\delta$) of CO; 169.5(s), 170.0(d, $J$ = 2.9 Hz), 172.4(d, $J$ = 2.9 Hz), 173.8(s).

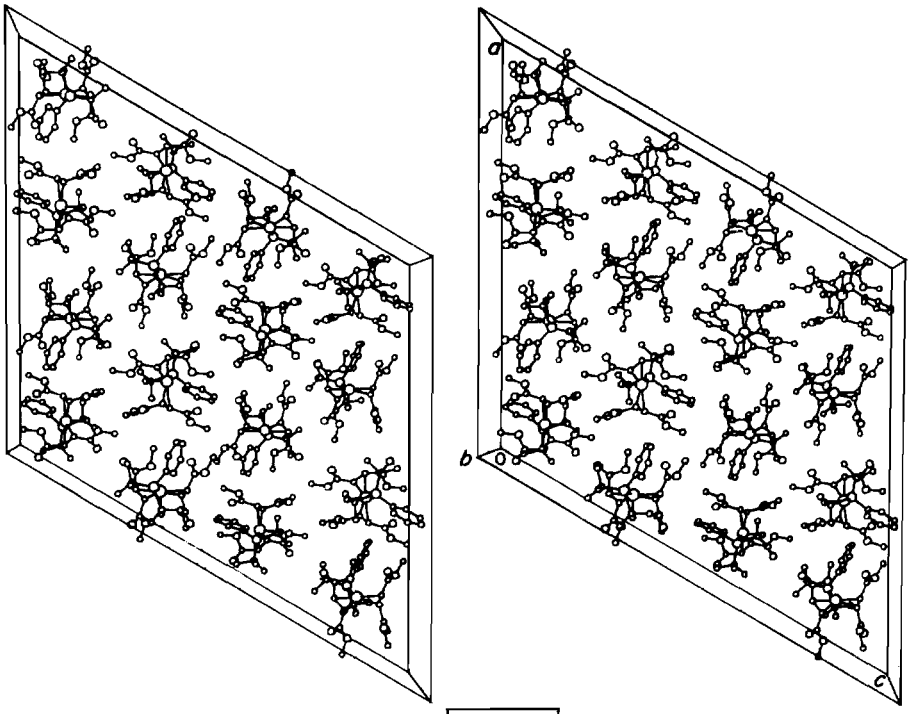



Fig. 1. Stereoview of the crystal structure of $Rh[CH_2CMe_2]PPh(t\text{-}Bu)](DF)_2$ (2).

TABLE III. Selected Bond Lengths (Å) and Angles (deg) for $Rh[CH_2CMe_2]PPh(t\text{-}Bu)](DF)_2$ (2).[a]

| Molecule I | | Molecule II | |
|---|---|---|---|
| Bond Lengths | | | |
| Rh(1)–P(1) | 2.362(4) | Rh(2)–P(2) | 2.375(4) |
| Rh(1)–C(2) | 2.09(2) | Rh(2)–C(28) | 2.12(1) |
| Rh(1)–A(1) | 2.02(2) | Rh(2)–A(2) | 2.04(2) |
| Rh(1)–B(1) | 2.04(2) | Rh(2)–B(2) | 2.06(2) |
| Rh(1)–O(5) | 2.53(1) | Rh(2)–O(13) | 2.545(9) |
| Rh(1)–C(17) | 2.16(1) | Rh(2)–C(43) | 2.19(2) |
| Rh(1)–C(18) | 2.11(1) | Rh(2)–C(44) | 2.13(2) |
| Rh(1)–C(23) | 2.15(1) | Rh(2)–C(49) | 2.18(2) |
| Rh(1)–C(24) | 2.17(1) | Rh(2)–C(50) | 2.18(2) |
| P(1)–C(1) | 1.91(2) | P(2)–C(27) | 1.95(1) |
| P(1)–C(3) | 1.83(1) | P(2)–C(29) | 1.83(2) |
| P(1)–C(9) | 1.92(2) | P(2)–C(35) | 1.92(2) |
| C(1)–C(2) | 1.52(2) | C(27)–C(28) | 1.58(2) |
| C(1)–C(13) | 1.57(2) | C(27)–C(39) | 1.52(2) |
| C(1)–C(14) | 1.50(2) | C(27)–C(40) | 1.48(3) |
| C(15)–O(1) | 1.45(2) | C(41)–O(9) | 1.48(2) |
| C(16)–C(17) | 1.50(2) | C(42)–C(43) | 1.47(2) |
| C(16)–O(1) | 1.31(2) | C(42)–O(9) | 1.33(2) |
| C(16)–O(3) | 1.22(2) | C(42)–O(11) | 1.24(2) |
| C(17)–C(18) | 1.41(2) | C(43)–C(44) | 1.42(2) |
| C(18)–C(19) | 1.48(2) | C(44)–C(45) | 1.49(2) |
| C(19)–O(2) | 1.39(2) | C(45)–O(10) | 1.37(2) |
| C(19)–O(4) | 1.20(2) | C(45)–O(12) | 1.22(2) |
| C(20)–O(2) | 1.49(2) | C(46)–O(10) | 1.46(2) |
| C(21)–O(5) | 1.48(2) | C(47)–O(13) | 1.50(2) |
| C(22)–C(23) | 1.49(2) | C(48)–C(49) | 1.48(2) |
| C(22)–O(5) | 1.33(1) | C(48)–O(13) | 1.38(3) |
| C(22)–O(7) | 1.21(2) | C(48)–O(15) | 1.21(2) |

*(continued overleaf)*

TABLE III *(continued)*

| Molecule I | | Molecule II | |
|---|---|---|---|
| C(23)–C(24) | 1.42(2) | C(49)–C(50) | 1.46(2) |
| C(24)–C(25) | 1.48(2) | C(50)–C(51) | 1.51(2) |
| C(25)–O(6) | 1.31(2) | C(51)–O(14) | 1.36(2) |
| C(25)–O(8) | 1.22(2) | C(51)–O(16) | 1.19(2) |
| C(26)–O(6) | 1.48(2) | C(52)–O(14) | 1.44(2) |
| Bond Angles | | | |
| P(1)–Rh(1)–C(2) | 69.5(4) | P(2)–Rh(2)–C(28) | 70.1(4) |
| P(1)–Rh(1)–O(5) | 107.0(3) | P(2)–Rh(2)–O(13) | 106.6(2) |
| C(2)–Rh(1)–O(5) | 164.2(4) | C(28)–Rh(2)–O(13) | 162.3(6) |
| A(1)–Rh(1)–P(1) | 118.0(6) | A(2)–Rh(2)–P(2) | 117.9(6) |
| A(1)–Rh(1)–C(2) | 94.0(7) | A(2)–Rh(2)–C(28) | 95.8(7) |
| A(1)–Rh(1)–O(5) | 101.0(7) | A(2)–Rh(2)–O(13) | 100.8(6) |
| A(1)–Rh(1)–B(1) | 126.8(8) | A(2)–Rh(2)–B(2) | 125.5(9) |
| B(1)–Rh(1)–P(1) | 115.1(6) | B(2)–Rh(2)–P(2) | 116.5(6) |
| B(1)–Rh(1)–C(2) | 103.0(7) | B(2)–Rh(2)–C(28) | 101.1(8) |
| B(1)–Rh(1)–O(5) | 63.9(6) | B(2)–Rh(2)–O(13) | 64.1(6) |
| C(1)–P(1)–C(3) | 113.9(7) | C(27)–P(2)–C(29) | 111.5(6) |
| C(1)–P(1)–C(9) | 112.3(7) | C(27)–P(2)–C(35) | 112.6(8) |
| C(3)–P(1)–C(9) | 100.4(7) | C(29)–P(2)–C(35) | 101.3(8) |
| P(1)–C(1)–C(2) | 95(1) | P(2)–C(27)–C(28) | 93.7(7) |
| P(1)–C(1)–C(13) | 109(1) | P(2)–C(27)–C(39) | 109(1) |
| P(1)–C(1)–C(14) | 121(1) | P(2)–C(27)–C(40) | 120(1) |
| C(2)–C(1)–C(13) | 110(1) | C(28)–C(27)–C(39) | 112(1) |
| C(2)–C(1)–C(14) | 113(1) | C(28)–C(27)–C(40) | 111(1) |
| C(13)–C(1)–C(14) | 109(1) | C(39)–C(27)–C(40) | 110(1) |
| Rh(1)–C(2)–C(1) | 107(1) | Rh(2)–C(28)–C(27) | 105.4(8) |
| C(17)–C(16)–O(1) | 114(1) | C(43)–C(42)–O(9) | 112(1) |
| C(17)–C(16)–O(3) | 125(1) | C(43)–C(42)–O(11) | 127(2) |
| O(1)–C(16)–O(3) | 121(1) | O(9)–C(42)–O(11) | 121(1) |
| C(16)–C(17)–C(18) | 117(1) | C(42)–C(43)–C(44) | 113(1) |
| C(17)–C(18)–C(19) | 118(1) | C(43)–C(44)–C(45) | 119(1) |
| C(18)–C(19)–O(2) | 111(1) | C(44)–C(45)–O(10) | 114(1) |
| C(18)–C(19)–O(4) | 128(1) | C(44)–C(45)–O(12) | 127(1) |
| O(2)–C(19)–O(4) | 121(2) | O(10)–C(45)–O(12) | 119(1) |
| C(23)–C(22)–O(5) | 112(1) | C(49)–C(48)–O(13) | 111(1) |
| C(23)–C(22)–O(7) | 124(1) | C(49)–C(48)–O(15) | 126(2) |
| O(5)–C(22)–O(7) | 124(2) | O(13)–C(48)–O(15) | 122(2) |
| C(22)–C(23)–C(24) | 117(1) | C(48)–C(49)–C(50) | 117(1) |
| C(23)–C(24)–C(25) | 116(1) | C(49)–C(50)–C(51) | 115(2) |
| C(24)–C(25)–O(6) | 113(1) | C(50)–C(51)–O(14) | 110(1) |
| C(24)–C(25)–O(8) | 125(1) | C(50)–C(51)–O(16) | 124(1) |
| O(6)–C(25)–O(8) | 122(1) | O(14)–C(51)–O(16) | 126(1) |
| C(15)–O(1)–C(16) | 120(1) | C(41)–O(9)–C(42) | 115(1) |
| C(19)–O(2)–C(20) | 116(1) | C(45)–O(10)–C(46) | 117(1) |
| C(21)–O(5)–C(22) | 117(1) | C(47)–O(13)–C(48) | 118(1) |
| C(25)–O(6)–C(26) | 117(1) | C(51)–O(14)–C(52) | 114(1) |

[a]A(1), A(2), B(1), and B(2) represent the center of coordinated olefinic bonds, C(17)–C(18), C(43)–C(44), C(23)–C(24), and C(49)–C(50), respectively.

the methylene carbon C(2) and methoxy O(5) atoms at the axial sites. Note that one of the DF molecules acts as a bidentate ligand through the C=C bond and the ester MeO group. The deviation of the Rh(1) atom from the trigonal plane P(1)–A(1)–B(1), where A(1) and B(1) represent the center of the coordinated olefinic bonds, is only 0.02(1) Å. The two olefins do not lie exactly in the equatorial plane; the C(17)–C(18) and C(23)–C(24) vectors make angles with the P(1)–A(1)–B(1) plane by 4.8 and 26.1°, respectively. The latter large angle is apparently due to the chelation. Despite this deviation forced by the chelation the propensity of the olefinic ligands to assume the parallel con-

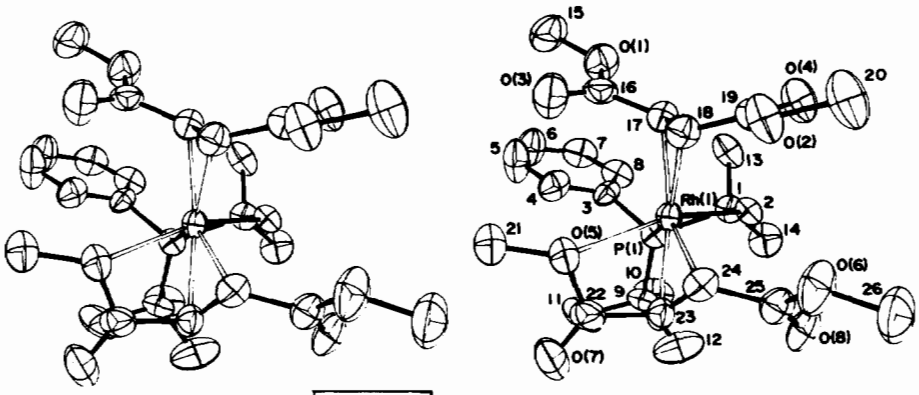



Fig. 2. Molecular structure of $Rh[CH_2CMe_2PPh(t\text{-}Bu)](DF)_2$ (2, molecule I) with the numbering scheme. The thermal ellipsoids are drawn at 50% probability level.

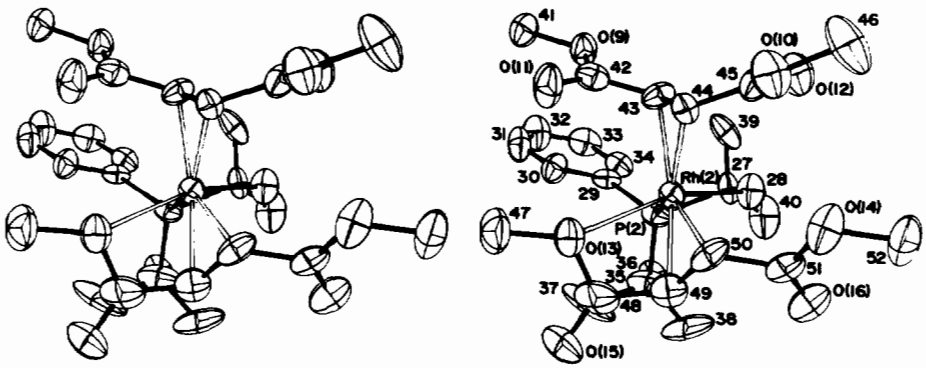



Fig. 3. Molecular structure of $Rh[CH_2CMe_2PPh(t\text{-}Bu)](DF)_2$ (2, molecule II) with the numbering scheme. The thermal ellipsoids are drawn at 50% probability level.

formation in the equatorial plane is evident. The angles involved in the trigonal plane, A(1)–Rh(1)–B(1) (126.8(8)°), P(1)–Rh(1)–A(1) (118.0(6)°), and P(1)–Rh(1)–B(1) (115.1(6)°), also differ substantially from the regular trigonal angle. The C(2)–Rh(1)–O(5) angle is 164.2(4)°, thus, the *z*-axis also deviates from linearity. The extensive deviation from the $C_3$ axis arises from the acute P(1)–Rh(1)–C(2) and B(1)–Rh(1)–O(5) angles of 69.5(4) and 63.9(6)°, respectively.

As evident from the acute P(1)–Rh(1)–C(2) angle, considerable strain is involved in the four-membered chelate ring $RhCH_2CMe_2P$. The angles at the P(1) (85.3(4)°) and C(1) atoms (95(1)°) are also less than the normal $sp^3$ value, while the angle at C(2) atom (107(1)°) is normal. A similar distortion of the ring $MCH_2CMe_2P$ was also found in $[MCH_2CMe_2P(t\text{-}Bu)_2(\mu\text{-}Cl)]_2$ (M = Pd, Pt) [20, 21] and $Ir(CNMe)[CH_2CMe_2P(t\text{-}Bu)C_6H_3(OMe)O]$-$[OC_6H_3(OMe)P(t\text{-}Bu)_2]$ [22], the P–M–C angle being 70.1(1), 70.1(2), and 67.3(2)° for the Pd, Pt, and Ir complexes, respectively. The enormous acute angle at the P(1) atom in the ring reflects in the expansion of the exocyclic angles, *e.g.* Rh(1)–P(1)–C(3) (118.3(4)°) and Rh(1)–P(1)–C(9) (126.6(4)°). A similar trend was also observed at the angles of the C(1) atom. It is to be noted that the inter-substituent angles both at the P(1) and C(1) atoms, C(3)–P(1)–C(9) (100.4(7)°) and C(13)–C(1)–C(14) (109(1)°) are not very much distorted.

The four-membered chelate ring in **2** deviates extensively from planarity, the deviation of the C(2) atom from the plane Rh(1)–P(1)–C(1) being 0.37(2) Å. This non-planarity is reflected in the large difference in the magnitude of $J_{H-P}$ (20.3 and 2.7 Hz) of the inequivalent $CH_2$ protons, indicating the rigidity of the ring conformation in solution. A similar deviation of the four-membered chelate ring was found in $[PdCH_2CMe_2P(t\text{-}Bu)_2(\mu\text{-}Cl)]_2$ [20]. The ring, however, is not rigid in solution as indicated by the chemical equivalence of two $CH_2$ protons.

The Rh(1)–P(1) distance of 2.362(4) Å is considerably longer than that (2.297(1) Å) found in the parent compound *trans*-$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$ [3]. The Rh(1)–C(2) bond length (2.09(2) Å) may be compared with Rh(I)–C($sp^2$) (~2.10 Å) [23, 24] and Rh(III)–C($sp^3$) distances (2.04–2.09 Å) [25]. As far as we know there is no example for the Rh(I)–$sp^3$ carbon bond distance so far reported.

The P(1)–C(1) distance (1.91(2) Å) in the four-membered ring is comparable with P(1)–C(9) (1.92(2) Å) and P(1)–C(t-Bu) distances (1.890–1.984 Å) found in *trans*-$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$ [3] and $M[PPh(t\text{-}Bu)_2]_2$ (M = Pt, Pd) [16]. The C(1)–C(2) bond length 1.52(2) Å is significantly shorter than the corresponding distance (1.606 Å) found in a similar ring in the Ir compound [22] cited above.

The non-bonded distance P(1)···C(2) (2.55(2) Å) in the ring is shorter than the distances P(1)···C(13) (2.84(2) Å), P(1)···C(14) (2.97(2) Å), and P(1)···C(12) (2.88(1) Å). This short non-bonded distance reflects the large $^2J_{P-C}$ (24 Hz) of the C(2) atom compared to those (0–4.4 Hz) found for the C(13), C(14), and C(12) atoms. The observed value of $^2J_{C-P}$ of the C(2) atom is much larger than the corresponding one bond coupling between the P(1) and C(1) atoms (7.6 Hz).

One of the remarkable features is the coordination of an ester methoxy group of the DF molecule. The Rh(1)–O(5) distance of 2.53(1) Å is much longer than the sum of the respective covalent radii (2.05 Å)† and is the longest so far reported (Table IV). The weak coordination could be due to the strong *trans*-influence of the $CH_2$ group and/or to the geometrical constraint of the DF ligand (*vide infra*).

Considerable distortions in the geometries are involved in the DF molecule coordinated through the C=C bond and a methoxy oxygen atom. The most prominent distortion is imposed upon the olefinic C(23) atom. Thus, the angle Rh(1)–C(23)–C(22) of 95.5(7)° is much smaller than the corresponding angle at C(24) (119(1)°), C(17) (115(1)°), and C(18) atoms (117.8(8)°) carrying free methoxy groups. In addition, a torsional angle Rh(1)–C(24)–C(23)–C(22) (87(1)°) is extremely small. The corresponding angles carrying free MeO groups (Table V) are in the range of 103–104° found for olefin complexes of Rh(I) [35] and Ir(I) [36, 37]. It is noteworthy that this type of torsional angle represents the degree of re-hybridization of olefinic carbon atom from $sp^2$ to $sp^3$ upon $\pi$-coordination [38]. As expected from the extremely small torsional angle Rh(1)–C(24)–C(23)–C(22), the torsional angle C(22)–C(23)–C(24)–C(25) (–159(1)°) of the chelated DF molecule is larger than that found for the other DF molecule free from MeO coordination (139(1)°). The coordination of the MeO oxygen atom is also reflected in the torsional angle O(5)–C(22)–C(23)–C(24) (–41(2)°), which is much different from those of the equivalent angles carrying free MeO groups (Table V).

Despite the large distortion imposed upon the olefinic C(23) atom, the geometry of the Rh–olefin triangle, *e.g.* C(23)–Rh(1)–C(24) (38.3(6)°) and Rh(1)–C(23)–C(24) (71.5(8)°), are normal and essentially equal for both DF ligands in **2** (Table III). The Rh(1)–C(23) distance (2.15(1) Å) is similar to the remaining Rh–C(olefin) lengths (2.11(1)–2.17(1) Å); compared with those values (2.00–2.12 Å) found in a number of olefin complexes of Rh(I) [39]. The two C=C distances in **2** (1.41(2), 1.42(2) Å) are also equal within experimental error and are not unusual (1.34–1.44 Å for Rh(I) olefin complexes [39].

The coordination of the methoxy oxygen atom rather than the carbonyl atom of the ester deserves comment since the latter type of coordination seems to be common, as found in Ru complexes, $Ru\dot{H}[\overline{CH{=}C(CH_3)C(\dot{O})}OC_4H_9](PPh_3)_3$ [40] and $Ru\dot{[}\overline{C(CO_2Me){=}CHC(\dot{O})}OMe](PPh_3)(\eta^5\text{-}C_5H_5)$ [41]. Inspection of the geometry around the coordinated methoxy O(5) atom reveals that the angle Rh(1)–O(5)–C(22) (84.2(9)°) deviates extensively from the regular $sp^3$ angle. If the chelation involves the carbonyl oxygen atom, even greater deviation from the normal $sp^2$ angle would occur. A rationale for the observed coordination of the MeO group, therefore, may be found in the steric reason. The larger radial part of the $sp^3$ orbital than that of the $sp^2$ orbital is a factor reducing the steric con-

†Since the covalent radius of Rh(I) is unavailable, it was estimated to be 1.36 Å by subtracting the covalent radius of Cl (0.94 Å) from the mean Rh(I)–Cl distance found in $RhCl(PPh_3)_3$ [28].

TABLE IV. Rh–O Distances.

| | Rh–O (Å) | Ref. |
|---|---|---|
| $Rh_2(OAc)_4(H_2O)_2$ | 2.301(3)($H_2O$) | 27 |
| $RhCl(H_2O)[C_4(CF_3)_4](AsMe_3)_2$ | 2.243(11) | 28 |
| $RhCl(H_2O)(COClC{=}CClCO)(PPhMe_2)_2$ | 2.28 | 29 |
| $RhCl_2[CH_2CH(CH_2OH)CH_2CH{=}CH_2]_2$ | 2.04(1) | 30 |
| $Rh(acac)(C_8H_{12})(C_4F_6)\cdot 3/2H_2O$ | 2.32($H_2O$) | 31 |
| $RhH_2(\eta^2\text{-}O_2COH)[P(i\text{-}Pr)_3]_2$ | 2.306(3), 2.279(2) | 32 |
| $Rh_2(\mu\text{-}\eta^1,\eta^2\text{-}O_2CO)(PPh_3)_5$ | 2.104(7)–2.138(7) | 33 |
| $Rh_2H_2(\mu\text{-}\eta^2,\eta^2\text{-}O_2CO)(PhC{\equiv}CPh)[P(i\text{-}Pr)_3]_3$ | 2.092(2)–2.324(2) | 6 |
| $\{\overline{Rh(CO)[Ph_2\dot{P}(CH_2)_2\dot{O}(CH_2)_2\dot{P}Ph_2]}\}PF_6$ | 2.112(8) | 34 |

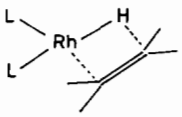
TABLE V. Torsional Angles (deg.) Involved in the Coordinated DF Molecules.

| Molecule I | | Molecule II | |
|---|---|---|---|
| $\phi$[Rh–C=C–C] | | | |
| Rh(1)–C(24)–C(23)–C(22) | 87(1) | Rh(2)–C(50)–C(49)–C(48) | −88(1) |
| Rh(1)–C(23)–C(24)–C(25) | 114(1) | Rh(2)–C(49)–C(50)–C(51) | −109(1) |
| Rh(1)–C(18)–C(17)–C(16) | −108(1) | Rh(2)–C(44)–C(43)–C(42) | 105(1) |
| Rh(1)–C(17)–C(18)–C(19) | −113(1) | Rh(2)–C(43)–C(44)–C(45) | 114(1) |
| $\phi$[C–C=C–C] | | | |
| C(16)–C(17)–C(18)–C(19) | 139(1) | C(42)–C(43)–C(44)–C(45) | −141(1) |
| C(22)–C(23)–C(24)–C(25) | −159(1) | C(48)–C(49)–C(50)–C(51) | 163(1) |
| $\phi$[O–C–C=C] | | | |
| O(2)C–(19)–C(18)–C(17) | −167(1) | O(10)–C(45)–C(44)–C(43) | 157(1) |
| O(1)–C(16)–C(17)–C(18) | −158(1) | O(9)–C(42)–C(43)–C(44) | 160(1) |
| O(6)–C(25)–C(24)–C(23) | 160(1) | O(14)–C(51)–C(50)–C(49) | −174(1) |
| O(5)–C(22)–C(23)–C(24) | −41(2) | O(13)–C(48)–C(49)–C(50) | 43(2) |

straint and the long C–O(Me) distance compared to that of C=O is also favorable for the MeO oxygen coordination.

Extended Hückel MO calculations on trigonal bipyramidal $d^8$ complexes predict that $\sigma$-donor ligands favor axial positions, while $\pi$-acids prefer parallel coordination in equatorial sites [42]. The molecular structure of **2** thus provides an example supporting the naive MO calculations. Although the chelating coordination of the DF molecule is not strong, as manifested from the long Rh–OMe distance, the preferred trigonal bipyramidal structure of **2** rather than square planar alternatives (**B** and **C**) is surprising. It appears that two electron-accepting olefinic ligands in the equatorial plane strongly demand the oxygen lone pair coordination, in spite of the steric constraint.

Finally, the molecular structure of **2** being established, the discussion on the reaction scheme leading to **2** instead of an insertion product is in order. The C-metallation observed in the reaction of P(t-Bu)$_3$ with $PtCl_2$ [43, 44] and [IrCl(cyclooctene)$_2$]$_2$ [45] occurs through an intramolecular oxidative addition of the methyl C–H bond of the tert-butyl substituent. Similarly the formation of **2** can be accounted for by an intermediacy of a hexa-coordinated dihydrido Rh(III) species, $RhH_2[CH_2CMe_2PPh(t\text{-}Bu)](DF)_2$. The presence of electron-accepting olefin ligands favors dihydrogen elemination rather than the insertion, as was the case for the reaction between *cis*-$PtH_2L_2$ and $\pi$-acids [46]. In the case of the less sterically-demanding ligand P(i-Pr)$_3$, the C-metallation of i-Pr groups was not observed, the product **1** being the normal adduct containing one olefin molecule. Consequently we would infer that the presence of bulky ligands provides a driving force to undergo the intramolecular C-metallation reaction leading to a less crowded molecule. Another reason why the expected insertion does not occur may be ascribed to a steric effect. The addition of a M–H species to an olefin occurs through a four center transition state [47]. An




approach of a bulky olefin DF to RhH[P(i-Pr)$_3$]$_3$ with concomitant dissociation of one P(i-Pr)$_3$ ligand to form the four center transition state would be severely hindered. This inference is supported by a facile ethylene insertion observed for *cis*-RhH($CH_2$=$CH_2$)[P(i-Pr)$_3$]$_2$ [48].

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