# From Methyl to Acetyl Complexes. An Example of Alkyl Migration in Heterotrinuclear Systems. Crystal and Molecular Structure of [{Rh($\mu$-pz)($\mu$-S$^t$Bu)I(COMe)P(OMe)$_3$}$_2$Pd]

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## Introduction

Oxidative addition of alkyl halides to low valent transition-metal complexes has proven to be a convenient way to form alkylmetal complexes which are of widespread use both as reagents and as isolable intermediates in organic synthesis.[1−3] The catalytic carbonylation of methanol to acetic acid is an industrial process where the key step is the oxidative addition reaction of methyl iodide to Rh(I) followed by methyl migration to generate a $\sigma$-acyl compound.[4,5]

In particular, oxidative addition reactions of halogenomethane ligands to systems containing nitrogen or sulfur donor ligands bridging homonuclear systems have been the subject of several investigations. The nature of these types of reactions appears to depend on the nature of the metal center and the bridging ligands. Formation of metal−metal bonds has been described in the addition of MeI to [Ir$_2$($\mu$-pz)$_2$(L)$_2$], L = COD, (CO)(PPh$_3$)[6,7] and [Ir$_2$($\mu$-S$^t$Bu)$_2$(CO)$_2$(PPh$_3$)$_2$][8] systems whereas acetyl derivatives have been isolated after alkyl migration in the [Rh$_2$($\mu$-S$^t$Bu)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] complex.[9] In this context, we have recently described the formation of [M$_2$($\mu$-pz)($\mu$-S$^t$Bu)(Me)I(CO)$_2${P(OMe)$_3$}$_2$] (M = Rh, Ir)[10,11] which present a single metal−metal bond as result of the addition of the methyl group to one metal centre and the iodide ligand to the other metal atom.

While continuing our studies concerning the preparation and properties of polynuclear complexes containing the Rh($\mu$-pz)($\mu$-S$^t$Bu)Pd($\mu$-pz)($\mu$-S$^t$Bu)Rh framework,[12] we have dealt with the formation of heterotrinuclear-acetyl derivatives. A study of a migration process of the alkyl group is described in this paper.

**Table 1.** Crystallographic Data for Complex **2b**

| | |
|---|---|
| mol formula | C$_{24}$H$_{48}$I$_2$N$_4$O$_8$P$_2$PdRh$_2$S$_2$ |
| mol wt | 1212.75 |
| cryst syst | monoclinic |
| space group | $P2_1/n$ |
| radiation ($\lambda$, Å) | Nb-filtered Mo K$\alpha$ (0.710 73) |
| $a$, Å | 9.671(4) |
| $b$, Å | 25.033(9) |
| $c$, Å | 17.214(7) |
| $\beta$, deg | 92.64(2) |
| $V$, Å$^3$ | 4163(3) |
| $Z$ | 4 |
| $D_{calcd}$, g cm$^{-3}$ | 1.935 |
| $F$(000) | 2352 |
| cryst dimens, mm | 0.15 × 0.22 × 0.28 |
| linear abs, cm$^{-1}$ | 29.14 |
| $R^a$ | 0.0420 |
| $R_w{}^b$ | 0.0342 |

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega(F_o)^2]^{1/2}$.

## Experimental Section

All reactions were carried out under nitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (carbonyl stretching region). Solvents were purified according to standard literature procedures and distilled under nitrogen prior to use. The compound [{Rh($\mu$-pz)($\mu$-S$^t$Bu)(CO)P(OMe)$_3$}$_2$Pd] (**1**) was prepared as described previously.[12] All other reagents were purchased from Aldrich and used as received. Infrared spectra were recorded in solution on a Perkin-Elmer 783 spectrophotometer. $^1$H- and $^{31}$P-{$^1$H} NMR spectra were carried out in CDCl$_3$ solution at room temperature on a Varian XL 300 spectrometer. $^{31}$P chemical shifts are positive downfield from external 85% H$_3$PO$_4$ in D$_2$O. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser.

**Preparation of [{Rh($\mu$-pz)($\mu$-S$^t$Bu)I(Me)(CO)P(OMe)$_3$}$_2$Pd] (2a).** An excess of MeI (0.051 mL) was added to a solution of complex [{Rh($\mu$-pz)($\mu$-S$^t$Bu)(CO)(P(OMe)$_3$)}$_2$Pd] (**1**) (150 mg, 0.161 mmol) in dichloromethane. The mixture was stirred at room temperature for 2 h while the color changed from yellow to orange and the IR spectrum showed no starting material. The solvent and the MeI in excess were removed under reduced pressure to 1 mL. Addition of hexane (15 mL) gave an orange solid which was filtered off, washed with hexane, and dried under vacuum (117 mg, 60%). Anal. Calcd for C$_{24}$H$_{48}$N$_4$I$_2$O$_8$P$_2$Rh$_2$S$_2$Pd: C, 23.75; H, 3.46; N, 4.61. Found: C, 23.81; H, 3.50; N, 4.66. IR (cm$^{-1}$, CH$_2$Cl$_2$); $\nu$ (CO) 2075. $^{31}$P{$^1$H}NMR (CDCl$_3$): $\delta$ 108.1 (d, $J_{RhP}$ = 160 Hz). $^1$H NMR (CDCl$_3$): $\delta$ 1.30 (s, S$^t$Bu), 1.56 (s, Me), 3.75 (d, $^3J_{PH}$ = 11.2 Hz, P(OMe)$_3$), 6.15 (vt, $^3J_{HH}$ = 2.2 Hz, H$^4$ pz), 8.10 (d, $^3J_{HH}$ = 2.2 Hz, H$^3$ Hpz), 9.15 (d, $^3J_{HH}$ = 2.2 Hz, H$^5$ pz).

**Preparation of [{Rh($\mu$-pz)($\mu$-S$^t$Bu)I(COMe)(P(OMe)$_3$)}$_2$Pd] (2b).** Compound **2b** was prepared by the same method described for compound **2a**, starting from complex **1** (150 mg, 0.161 mmol) and MeI (0.051 mL) and stirring the mixture during 36 hours (137 mg, 70%). Anal. Calcd for C$_{24}$H$_{48}$N$_4$I$_2$O$_8$P$_2$Rh$_2$S$_2$Pd: C, 23.75; H, 3.46; N, 4.61. Found: C, 23.68; H, 3.40; N, 4.63. IR (cm$^{-1}$, CH$_2$Cl$_2$); $\nu$ (CO) 1720. $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta$ 112.6 (d, $J_{RhP}$ 202). $^1$H NMR (CDCl$_3$): $\delta$ 1.28 (s, S$^t$Bu), 2.66 (s, COMe), 3.83 (d, $^3J_{PH}$ = 10.8 Hz, P(OMe)$_3$), 6.27 (vq, $^5J_{PH}$ = 2.4 Hz, $^3J_{HH}$ = 2.2 Hz, H$^4$ pz), 8.22 (vt, $^4J_{PH}$ = 2.2 Hz, $^3J_{HH}$ = 2.2 Hz, H$^3$ pz), 9.21 (d, $^3J_{HH}$ = 2.2 Hz, H$^5$ pz).

**X-ray Crystal Structure Determination of [{Rh($\mu$-pz)($\mu$-S$^t$Bu)I-(COMe)P(OMe)$_3$}$_2$Pd] (2b).** Crystals of **2b** suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into a CH$_2$Cl$_2$ solution of **2b**. The crystallographic data are summarized in Table 1. Data were collected at room temperature on a Siemens AED

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**Table 2.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å$^2$ × $10^4$) with Esd's in Parentheses for the Non-Hydrogen Atoms of Complex **2b**

| | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Rh(1) | 1179(1) | 144(1) | 2653(1) | 350(1) |
| Rh(2) | −1747(1) | −2165(1) | 3506(1) | 358(1) |
| Pd | −376(1) | −1141(1) | 2240(1) | 321(1) |
| I(1) | 702(1) | 1162(1) | 3038(1) | 626(2) |
| I(2) | −1211(1) | −3019(1) | 4417(1) | 659(2) |
| S(1) | 1706(1) | −685(1) | 2120(1) | 355(4) |
| S(2) | −2429(1) | −1589(1) | 2486(1) | 368(4) |
| P(1) | 3404(1) | 260(1) | 3036(1) | 420(5) |
| P(2) | −3864(2) | −2160(1) | 3992(1) | 469(5) |
| O(1) | 4221(4) | −287(1) | 3145(2) | 553(15) |
| O(2) | 3861(4) | 600(2) | 3783(2) | 647(16) |
| O(3) | 4221(4) | 562(2) | 2409(2) | 748(18) |
| O(4) | −4795(4) | −2642(2) | 3662(3) | 817(19) |
| O(5) | −4088(5) | −2237(2) | 4875(3) | 961(22) |
| O(6) | −4740(4) | −1665(2) | 3720(2) | 636(16) |
| O(7) | 1465(4) | −496(2) | 3999(2) | 654(17) |
| O(8) | −1849(4) | −1163(2) | 4221(2) | 673(17) |
| N(1) | −1363(4) | −449(2) | 1966(2) | 366(14) |
| N(2) | −815(4) | 49(2) | 2129(2) | 386(14) |
| N(3) | 650(4) | −1825(2) | 2497(2) | 365(13) |
| N(4) | 192(4) | −2206(2) | 2993(2) | 375(14) |
| C(1) | −1680(5) | 415(2) | 1812(3) | 466(19) |
| C(2) | −2786(6) | 168(2) | 1443(3) | 535(21) |
| C(3) | −2552(5) | −376(2) | 1548(3) | 500(20) |
| C(4) | 1827(5) | −1998(2) | 2215(3) | 455(19) |
| C(5) | 2157(5) | −2490(2) | 2516(3) | 504(20) |
| C(6) | 1118(5) | −2604(2) | 2999(3) | 467(19) |
| C(7) | 3399(8) | 494(3) | 4526(4) | 987(36) |
| C(8) | 4733(11) | 1067(3) | 2419(6) | 1812(65) |
| C(9) | 5685(5) | −322(3) | 3307(4) | 696(26) |
| C(10) | −5252(8) | −3091(3) | 4006(4) | 1048(38) |
| C(11) | −3364(7) | −2027(3) | 5516(4) | 873(32) |
| C(12) | −6140(6) | −1552(3) | 3949(4) | 748(28) |
| C(13) | 1984(5) | −530(2) | 1061(3) | 467(19) |
| C(14) | 1138(7) | −917(3) | 545(3) | 790(28) |
| C(15) | 3503(6) | −608(3) | 968(4) | 863(32) |
| C(16) | 1593(7) | 39(2) | 861(3) | 811(29) |
| C(17) | −2872(6) | −2067(2) | 1665(3) | 486(20) |
| C(18) | −4405(6) | −2153(3) | 1677(4) | 860(32) |
| C(19) | −2166(9) | −2595(3) | 1769(5) | 1343(45) |
| C(20) | −2506(9) | −1823(3) | 911(4) | 1274(44) |
| C(21) | 727(5) | −188(2) | 3663(3) | 426(18) |
| C(22) | −644(5) | −14(2) | 3943(3) | 640(24) |
| C(23) | −1179(6) | −1553(2) | 4177(3) | 461(19) |
| C(24) | 206(6) | −1626(2) | 4620(3) | 612(23) |

[a] Equivalent Isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

single-crystal diffractometer using niobium-filtered Mo Kα radiation and the $\theta/2\theta$ scan mode. All reflections with $\theta$ in the range 3−30° were measured; of 12 188 independent reflections, 8793, having $I > 2\sigma(I)$, were considered observed and used in the analysis. The individual profiles have been analyzed according to Lehmann and Larsen.[13] The intensity of one standard reflection was measured after 75 reflections as a general check on crystal and instrument stability; no significant change in the measured intensities was observed during the data collection. No correction of the absorption effect was applied. Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non hydrogen atoms. All hydrogen atoms were placed at their geometrically calculated positions (C−H = 0.96 Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 408 variables; after the last cycles, no parameters shifted by more than 0.90 esd. The biggest remaining peak in the final difference map was equivalent to about 0.82 e/Å$^3$. In the final cycles of refinement a weighting scheme, $w = 1/[\sigma^2(F_o)]$, was used. The atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 14.

All calculations were carried out on the GOULD POWERNODE 6040 and ENCORE 91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[15] The final atomic coordinates for the non hydrogen atoms are given in Table 2. The atomic coordinates of the hydrogen atoms are given in Table SI, the thermal parameters in Table SII.

## Results and Discussion

The reaction of the recently reported heterobridged compound [{Rh($\mu$-pz)($\mu$-S$^t$Bu)(CO)P(OMe)$_3$}$_2$Pd] (**1**)[12] with methyl iodide in excess and at room temperature occurs slowly and it is easily monitored by infrared and NMR spectroscopy.

The addition of methyl iodide to a dichloromethane solution of compound **1**, with a CH$_3$I/Rh = 5/1 molar ratio, progressively causes the colour of the solution to change from yellow to orange. The infrared spectrum shows the band at 1995 cm$^{-1}$ of the starting material disappearing while being shifting to higher frequencies. After 2 h of stirring, only one band at 2075 cm$^{-1}$, corresponding to terminal carbonyl ligands, is observed indicating the complete oxidation of compound **1**. These data, together with the presence of only one doublet ($\delta$ = 108.1 ppm, $J_{RhP}$ = 160 Hz), in the $^{31}$P{$^1$H}-NMR spectrum of this solution, indicate that both rhodium centers are equivalent and this is only possible after addition of one molecule of MeI to each rhodium atom. The presence of only terminal-carbonyl ligands and the $^{103}$Rh−$^{31}$P coupling constant value, within the range observed for other rhodium(III) complexes,[11,16] allow us to formulate as [{Rh($\mu$-pz)($\mu$-S$^t$Bu)I(Me)(CO)(P(OMe)$_3$)}$_2$Pd] (**2a**) the compound formed in this reaction. One of the possible molecular structures which may be proposed for compound **2a** is shown in Scheme 1.

If we allow a longer reaction time we observe at 1720 cm$^{-1}$ the formation of a band of low intensity from acetyl groups while the band at 2075 cm$^{-1}$ decreases. This observation is in accord with the $^{31}$P{$^1$H}-NMR spectrum which shows the signals previously commented together with a new doublet which appears at lower field ($\delta$ = 112.6 ppm, $J_{RhP}$ = 202 Hz). The increase of the $J_{RhP}$ coupling constant agrees with the formation of an acetyl derivative.

Finally, after 36 h of reaction, the spectroscopic data indicate the only presence in solution of the heterotrinuclear acetyl derivative **2b**. On the basis of the data commented above we propose the formation of a symmetrical compound wherein each rhodium centre is carrying one iodide and one acetyl group. Compound **2b** is correctly described as a Rh(III)• •Pd(II)• •Rh(III) system. After evaporation of the solvent and MeI in excess and by addition of hexane, an orange compound analyzing as [{Rh($\mu$-pz)($\mu$-S$^t$Bu)I(COMe){P(OMe)$_3$}$_2$Pd] (**2b**) is obtained.

The reaction involving [{Rh($\mu$-pz)($\mu$-S$^t$Bu)(CO)P(OMe)$_3$}$_2$Pd] and methyl iodide can be interpreted on the basis of an oxidative addition of a molecule of CH$_3$I to each rhodium center in complex **1**. Although the kinetic product of this reaction may well contain *trans*-adducts, we consider the acetyl derivative **2b** to arise from *cis*-migration of a methyl group in isomer **2a**,

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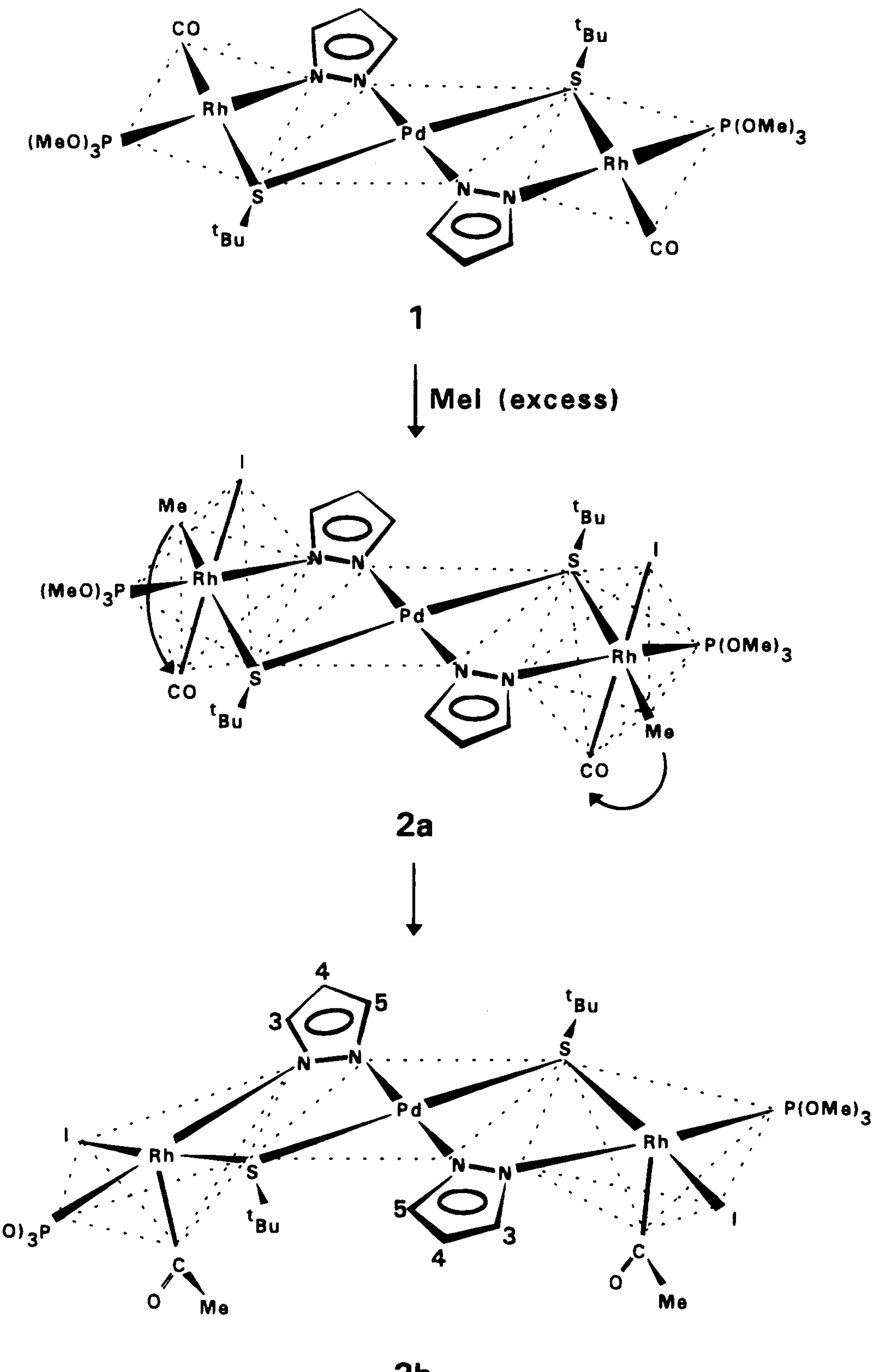
**Scheme 1**



as indicated in Scheme 1. It is interesting to point out the different behavior in analogue binuclear systems as M($\mu$-pz)($\mu$-S$^t$Bu)M (M = Rh, Ir) that no acetyl compounds were detected. In these cases the formation of a metal–metal bond has been explained by an heterolytically addition of the iodide and of the methyl groups.[10,11]

The crystal structure of **2b**, determined by an X-ray diffraction study, is shown in Figure 1 together with the atomic numbering scheme; selected bond distances and angles are given in Table 3. The trinuclear complex displays a Rh(1)PdRh(2) bent chain in which the Rh(1)Pd and Rh(2)Pd couples, at distances of 3.608(3) and 3.653(3) Å respectively (excluding any metal–metal interaction), are connected by a double bridge, with a pyrazolate ligand bridging through the two N atoms, and a S$^t$-Bu ligand through the S atom. Each Rh metal completes its coordination with one iodine atom and one carbon atom from

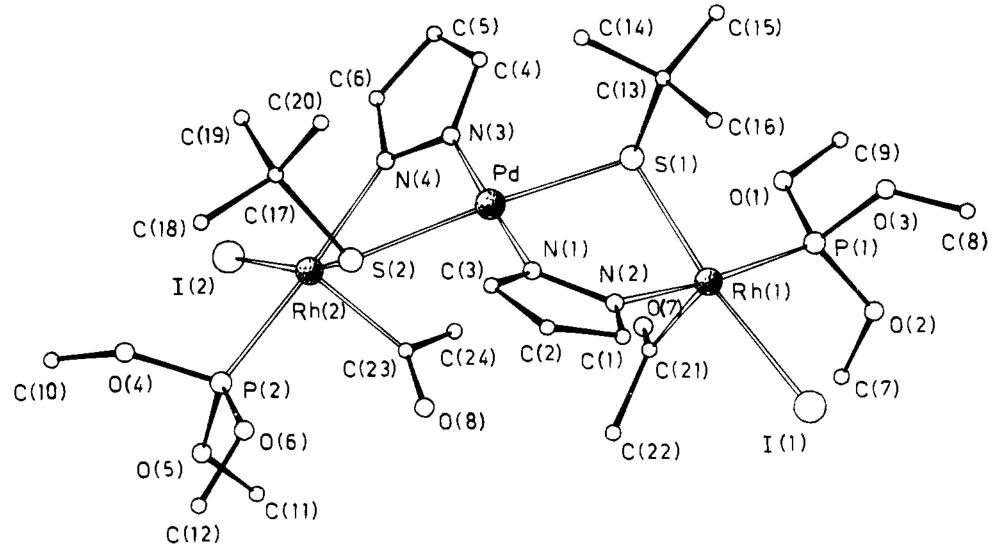


**Figure 1.** Perspective view of the molecular structure of the complex $[\{Rh(\mu\text{-pz})(\mu\text{-S}^t\text{Bu})I(COMe)(P(OMe)_3)\}_2Pd]$ (**2b**), showing the atomic numbering scheme.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for Complex **2b**

| | | | |
|---|---|---|---|
| Rh(1) − I(1) | 2.679(4) | Rh(1) − S(1) | 2.335(3) |
| Rh(1) − P(1) | 2.240(2) | Rh(1) − N(2) | 2.104(4) |
| Rh(1) − C(21) | 1.994(6) | Rh(2) − I(2) | 2.688(3) |
| Rh(2) − S(2) | 2.343(3) | Rh(2) − P(2) | 2.247(2) |
| Rh(2) − N(4) | 2.112(4) | Rh(2) − C(23) | 1.981(6) |
| Pd − S(1) | 2.332(2) | Pd − S(2) | 2.336(2) |
| Pd − N(1) | 2.023(5) | Pd − N(3) | 2.018(5) |
| S(1) − C(13) | 1.895(6) | S(2) − C(17) | 1.886(6) |
| P(1) − O(1) | 1.588(4) | P(1) − O(2) | 1.588(4) |
| P(1) − O(3) | 1.562(4) | P(2) − O(4) | 1.594(5) |
| P(2) − O(5) | 1.557(6) | P(2) − O(6) | 1.561(5) |
| O(7) − C(21) | 1.183(7) | O(8) − C(23) | 1.176(7) |
| N(1) − N(2) | 1.378(7) | N(1) − C(3) | 1.341(6) |
| N(2) − C(1) | 1.340(7) | N(3) − N(4) | 1.367(6) |
| N(3) − C(4) | 1.330(6) | N(4) − C(6) | 1.339(7) |
| C(1) − C(2) | 1.366(7) | C(2) − C(3) | 1.391(7) |
| C(4) − C(5) | 1.368(7) | C(5) − C(6) | 1.364(7) |
| C(21) − C(22) | 1.496(7) | C(23) − C(24) | 1.521(8) |
| I(1)−Rh(1)−C(21) | 97.7(2) | I(1)−Rh(1)−N(2) | 92.8(2) |
| I(1)−Rh(1)−P(1) | 88.7(1) | I(1)−Rh(1)−S(1) | 170.4(1) |
| N(2)−Rh(1)−C(21) | 95.4(2) | P(1)−Rh(1)−C(21) | 92.5(2) |
| S(1)−Rh(1)−C(21) | 91.9(2) | S(1)−Rh(1)−N(2) | 86.8(1) |
| S(1)−Rh(1)−P(1) | 90.4(1) | I(2)−Rh(2)−C(23) | 103.5(2) |
| I(2)−Rh(2)−N(4) | 93.1(1) | I(2)−Rh(2)−P(2) | 86.7(1) |
| N(4)−Rh(2)−C(23) | 93.1(2) | P(2)−Rh(2)−C(23) | 90.7(2) |
| S(2)−Rh(2)−C(23) | 91.3(2) | S(2)−Rh(2)−N(4) | 86.6(1) |
| S(2)−Rh(2)−P(2) | 92.6(1) | S(2)−Pd−N(3) | 88.1(1) |
| S(2)−Pd−N(1) | 93.3(2) | S(1)−Pd−N(3) | 91.0(2) |
| S(1)−Pd−N(1) | 87.7(1) | Rh(1)−S(1)−Pd | 101.3(1) |
| Pd−S(1)−C(13) | 110.3(2) | Rh(1)−S(1)−C(13) | 103.8(2) |
| Rh(2)−S(2)−Pd | 102.6(1) | Pd−S(2)−C(17) | 109.5(2) |
| Rh(2)−S(2)−C(17) | 102.6(2) | Rh(1)−P(1)−O(3) | 111.6(2) |
| Rh(1)−P(1)−O(2) | 122.4(2) | Rh(1)−P(1)−O(1) | 112.9(2) |
| O(2)−P(1)−O(3) | 99.8(2) | O(1)−P(1)−O(3) | 103.6(2) |
| O(1)−P(1)−O(2) | 104.4(2) | Rh(2)−P(2)−O(6) | 112.6(2) |
| Rh(2)−P(2)−O(5) | 122.2(2) | Rh(2)−P(2)−O(4) | 111.9(2) |
| O(5)−P(2)−O(6) | 107.0(3) | O(4)−P(2)−O(6) | 101.8(3) |
| O(4)−P(2)−O(5) | 98.8(3) | Rh(1)−C(21)−O(7) | 123.1(4) |
| O(7)−C(21)−C(22) | 123.8(5) | Rh(1)−C(21)−C(22) | 113.1(3) |
| Rh(2)−C(23)−O(8) | 122.7(4) | O(8)−C(23)−C(24) | 122.8(5) |
| Rh(2)−C(23)−C(24) | 114.4(4) | | |

the acetyl group. Each Rh atom is in a square pyramidal arrangement being bound to one S atom from S$^t$Bu ligand, to one N atom from the pyrazolate ligand, to one iodine atom, to a P atom from the P(OMe)$_3$ ligand at the four basal vertices and to one carbon atom from the acetyl group at the apex of the pyramid [Rh−C bond distances of 1.994(6) and 1.981(6) Å]. The central Pd atom is in a square planar arrangement involving two N atoms from the two pyrazolate ligands and the two S atoms.

The structure of **2b** can be compared with that of the complex $[\{Rh(\mu\text{-pz})(\mu\text{-S}^t\text{Bu})(CO)_2\}_2Pd]$, strictly related to the starting complex **1**,[12] in which the RhPdRh chain is linear [the Rh···Pd separations are 3.686(1) Å] and the coordination is square planar for all three metal atoms. The Pd−N [2.007(7) Å] and Pd−S [2.317(2) Å] bond distances are comparable to those of **2b** [2.018(5) and 2.023(5) Å] as well as the Pd−S ones [2.332(2) and 2.336(2) Å], the Pd atom maintaining the same square planar coordination. Even if the coordination around the Rh atoms (and the oxidation state) changes from square planar to square pyramidal in **2b**, the Rh−S [2.349(2) Å] bond distances are very similar to those of **2b** [2.335(3) and 2.343(3) Å], whereas the Rh−N [2.039(5) Å] bond distances are much shorter than those of found in **2b** [2.104(4) and 2.112(4) Å].

The $^1$H NMR spectrum of CDCl$_3$ solution of **2b** is fully consistent with the molecular structure observed in the solid state. The phosphite protons appear as one doublet at 3.83 ppm with $^3J_{PH}$ coupling of 10.8 Hz, indicating the equivalence of both phosphorus donor ligands. The protons of the acetyl groups appear as one singlet at 2.66 ppm. The tert-butyl protons of the thiolate bridging ligands exhibit one singlet at 1.28 ppm. The range within 6−9 ppm provides key information about the terminal ligands disposition. The presence of one virtual quartet (H$^4$) at 6.27 ppm indicates that the H$^4$ pyrazolate proton is coupled with the phosphorus atom of one trimethyl phosphite ligand ($^5J_{PH}$ = 2.4 Hz) and with the H$^3$ and H$^5$ pyrazolate protons ($^3J_{HH}$ = 2.2 Hz) and is indicative of a mutual *trans* disposition of the phosphite ligands with respect the pyrazolate bridging groups,[8,17] as observed in the solid state. The H$^3$ pyrazolate proton resonates at 8.22 ppm (vt, $^4J_{PH}$ = 2.2 Hz, $^3J_{HH}$ = 2.2 Hz) and from H$^5$ appears one doublet at 9.21 ppm ($^3J_{HH}$ = 2.2 Hz). The absence of $J_{PH}$ for H$^5$ could indicate that this proton is nearer to the palladium atom than H$^3$ (see Scheme 1, compound **2b**).

Studies of oxidative additions of alkyl halides to low valent complexes of rhodium and iridium have mainly focused on mononuclear species.[1−6,18−20] Fewer studies have involved the

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reaction of methyl iodide with binuclear rhodium or iridium complexes.[6-11,21,22] The present paper reports an interesting methylation process which deals with a MeOC$-$Rh$^{III}\cdots$Pd$^{II}\cdots$Rh$^{III}-$COMe system. To our knowledgement this is the first example described of *cis*-alkyl migration in heterotrinuclear rhodium complexes. The results presented confirm the high stability of the five-membered cyclic core Rh(N$-$N)(S)Pd(N$-$N)(S)Rh, which is retained in the oxidized compounds **2a** and **2b**.

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**Supplementary Material Available:** Coordinates for the hydrogen atoms (Table SI), anisotropic thermal parameters for the non-hydrogen atoms (Table SII), complete bond distances and angles (Table SIII), and crystallographic data (Table SIV) (6 pages). Ordering information is given on any current masthead page.

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