

Notes

A Convenient Synthesis and Molecular Structure of $\text{Ru}(\text{CO})_3[\text{Ph}_2\text{PN}(i\text{-Bu})\text{PPh}_2\text{-P}, \text{P}]$

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$\text{Ru}(\text{CO})_3[\text{Ph}_2\text{PN}(i\text{-Bu})\text{PPh}_2\text{-P}, \text{P}]$ was conveniently obtained by the reaction of $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ with $\text{Ph}_2\text{PN}(i\text{-Bu})\text{PPh}_2$ and CO in the presence of Zn powder under mild conditions. The crystal and molecular structure was determined by X-ray diffraction. This compound possesses a distorted trigonal bipyramidal configuration.

Keywords Synthesis, molecular structure, $\text{Ru}(\text{CO})_3[\text{Ph}_2\text{PN}(i\text{-Bu})\text{PPh}_2\text{-P}, \text{P}]$

Under mild conditions we have obtained some mono- or di-metal carbonyls containing phosphine ligand by the reductive carbonylation of metal halides.¹⁻⁴ We now extend this method to ruthenium compound to give a convenient preparation of $\text{Ru}(\text{CO})_3[\text{Ph}_2\text{PN}(i\text{-Bu})\text{PPh}_2]$. Only a few preparation methods for phosphine containing monoruthenium(0) carbonyl compounds were known. Collman and Poper firstly reported the preparation of *trans*- $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ by two-step reactions of RuCl_3 with CO and PPh_3 through $\text{RuCl}_2(\text{CO})_{2-n}$ intermediate at high pressure (60 psi) and elevated temperature (100°C).⁵ After this Pomeroy *et al.* developed two methods of preparation of $\text{Ru}(\text{CO})_4[\text{P}(\text{OCH}_3)_3]$ and $\text{Ru}(\text{CO})_3[\text{P}(\text{OCH}_3)_3]_2$ from $\text{Ru}_3(\text{CO})_{12}$ and $\text{P}(\text{OCH}_3)_3$ at high pressure (80 atm.) and temperature.⁶ Using the same method Pomeroy also obtained $\text{Ru}(\text{CO})_4(\text{AsPh}_3)$ compound.⁷ Ahmad *et al.* gave the preparation of *trans*- $\text{Ru}(\text{CO})_3(\text{PPh}_2)_2$ from RuCl_3 by reaction with polyaldehyde in the presence of PPh_3 .⁸

Recently, $\text{Ru}(\text{CO})_3[\text{Ph}_2\text{PN}(\text{Et})\text{PPh}_2\text{-P}, \text{P}]$ has been formed from $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ph}_2\text{PN}(\text{Et})\text{PPh}_2$ by a

photochemical method.⁹ We gave a two-step method for the preparation of $\text{Ru}(\text{CO})_3(\text{Ph}_2\text{Ppy})_2$.¹⁰

A dichloromethane/tetrahydrofuran solution of $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ was treated with diphosphazane $\text{Ph}_2\text{PN}(i\text{-Bu})\text{PPh}_2$ under an atmosphere of carbon monoxide at room temperature to give the ruthenium complex $\text{Ru}(\text{CO})_3[\text{Ph}_2\text{PN}(i\text{-Bu})\text{PPh}_2]$ (42%). The IR spectrum consisted of three absorption peaks assigned to $\nu(\text{CO})$ at 2050 (m), 1994 (s) and 1955 (m) cm^{-1} , which show the three carbonyls having C_{3v} symmetry. The ³¹P NMR spectrum revealed a single peak at 70.40.

The molecular structure with selected bond distances and bond angles of this compound determined by X-ray diffraction study is shown in Fig. 1. The Ru atom possesses a distorted trigonal bipyramidal configuration with one P atom in the axial position and the other P atom in the equatorial position. P(2)-Ru(1)-C(2) angle is 161.9°. C(1)/C(3)/P(1)/Ru basically lies in one plane. The summation of angles P(1)-Ru(1)-C(3) (117.6°), C(1)-Ru(1)-P(1) (122.7°) and C(1)-Ru(1)-C(3) (118.6°) is 358.9°. The structure may be compared to that of $\text{Ru}(\text{CO})_4[\text{P}(\text{OCH}_3)_3]$ ⁵ or $\text{Ru}(\text{CO})_4(\text{AsPh}_3)$ ⁷ in which the coordination of Ru ion is trigonal bipyramidal with $\text{P}(\text{OCH}_3)_3$ and AsPh_3 in axial positions. The average Ru—P distance in our compound (0.2345 nm) is longer than the value of 0.2309 nm in $\text{Ru}(\text{CO})_4[\text{P}(\text{OCH}_3)_3]$. The average Ru—C distance of 0.1870 nm is shorter than the value of 0.1933 nm and the C—O distance of 0.1170 nm is longer than the value of 0.1130 nm. These results show that the two

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phosphorus ligands possess better π -acceptor character. Therefore the σ -donor character of the C atom in carbonyls increases, the Ru—C bonds are strengthened and the C—O bond weakened. The dihedral angle between P—Ru—P and P—N—P is 2.6° .

We failed to obtain the analogous ruthenium complexes of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm), $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe) ligands by the same method. The ligand $\text{Ph}_2\text{PN}(i\text{-Bu})\text{PPh}_2$ is a stronger π -acid than dppm and dppe¹¹ and a stronger back-donating $d\pi\text{-}\sigma^*$ could be formed with the Ru(0) atom which is possible reason responsible for the formation of the new complex.

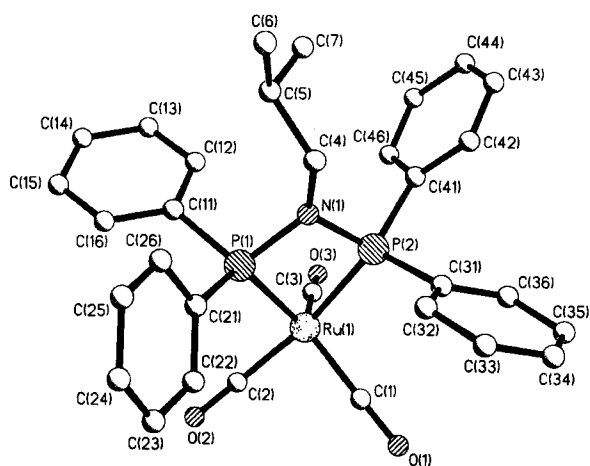


Fig. 1 Molecular structure of the title compound.

Crystal data: $\text{Ru}(\text{CO})_3[\text{Ph}_2\text{PN}(i\text{-Bu})\text{PPh}_2]$, $\text{C}_{31}\text{H}_{29}\text{NO}_3\text{P}_2\text{Ru}$, $M = 626.6$, triclinic, space group $P1$, $a = 1.8001(5)$, $b = 0.883(2)$, $c = 1.9684(7)$ nm, $\alpha = 89.95(3)^\circ$, $\beta = 104.35(3)^\circ$, $\gamma = 104.23(2)^\circ$; $V = 2.936$ nm³ and $Z = 4$. $\mu(\text{Mo K}\alpha) = 6.61$ cm⁻¹. Intensity data in the range $2 \leq \theta \leq 22$ were collected using a

$\omega/2\theta$ scan technique. Absorption corrections were applied. A total of 7458 unique reflections were collected of which 5095, with $I \geq 3\sigma(I)$, were used for all calculations.

The structure was solved by direct methods. Full-matrix squares refinement converged to $R = 0.067$ and $R_w = 0.078$.

A table of the atomic coordinates and a full list of bond lengths and angles has been deposited at the Cambridge Crystal Graphical Data Centre.

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