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Unexpected Coexistence of Isomeric Forms and Unusual Structures of $Ru(CO)_2L_3$[‖]

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One well-accepted principle for a five-coordinate d^8 molecule, and one which is broadly consistent with experiment, is that the trigonal bipyramidal structure (TBP) is preferred, and that strong π-acid ligands occupy equatorial sites.[1] For example, in the case of $Fe(CO)_2L_3$ (L = $P(OMe)_3$, cone angle 107°, and $P(OEt)_3$, cone angle 109°),[2] X-ray studies reveal a TBP structure with two equatorial carbonyl ligands.[3] We present here theoretical and experimental results dealing with significant exceptions to this idea.

Magnesium is a convenient two-electron reductant for *cis,cis-,trans*-$RuCl_2(CO)_2L_2$ in the presence of free L for 12 h at 25 °C in THF, giving $Ru(CO)_2L_3$. For L = PEt_3 (cone angle 132°)[2] the products have two CO stretching frequencies in the IR spectrum, with intensities indicative of a OC−Ru−CO angle around 130°.[4] This is thus consistent with the two CO ligands being at the equatorial sites of a TBP (bis equatorial geometry) as expected from a molecular orbital analysis.[1] A crystal structure of $Ru(CO)_2(PEt_3)_3$ confirms this structural conclusion from IR data. However, for the P-*i*-Pr_2Me analog (cone angle 146°),[2b] the IR spectrum (see below) shows one strong absorption, indicative of a OC−Ru−CO angle of nearly 180° and consistent with an isomer with *trans* carbonyls, i.e., a bis axial isomer; this was also the conclusion regarding the only previously known $Ru(CO)_2L_3$ species, that with L = PPh_3 (cone angle 145°).[5] Thus, there appears to be a steric threshold beyond which phosphine/phosphine repulsions prevent a bis equatorial isomer, and lead to the bis axial isomer, where the P−Ru−P angles (120°) minimize such repulsions.

We originally thought that, by our choice of a quite bulky phosphine, we could overwhelm any (presumed) electronic preference for the bis equatorial isomer by the reduced phosphine/phosphine steric repulsions characteristic of the bis axial isomer. While plausible, this reasoning is now proven to be quite false, since the calculations with the sterically small PH_3 suggest that several isomers can be populated. ECP *ab initio* calculations[6] with geometry optimization of the possible isomers of $Ru(CO)_2(PH_3)_3$ has been performed at the MP2 level, within C_s symmetry, with a valence double-ζ quality basis set for all atoms[7] supplemented with polarization functions on C, O, and P.[8] Three minima have been located, and two are shown in Figure 1. All are essentially ideal TBP which differ by the site occupancy of the CO ligands, bis axial for **I** and bis equatorial for **II**.[9] Surprisingly, isomer **I** is calculated to be only 3.1 kcal/mol above **II**. At this point, it is clear that there is no significant intrinsic electronic preference for a CO ligand in any of the isomeric TBP forms for $Ru(CO)_2L_3$. The experimentally preferred isomer(s) can thus be determined solely by the steric interactions between phosphines. Steric hindrance is likely to be minimized in **I** (three P−Ru−P at 120°).

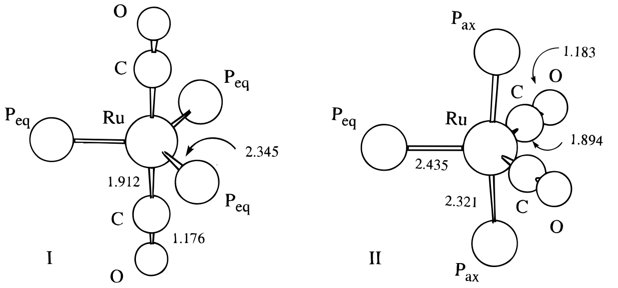

Figure 1. Two *ab initio* optimized geometries for $Ru(CO)_2(PH_3)_3$. For **I**, $\angle C-Ru-C = 178.6°$ and $\angle P-Ru-P = 120.0°$ (average). For **II**, $\angle C-Ru-C = 128.5°$, $\angle P_{ax}-Ru-P_{ax} = 174.1°$, and $\angle P_{eq}-Ru-P_{ax} = 92.8°$.

Stimulated by these results, we reexamined our IR spectra more carefully. This revealed that the two absorptions for $Ru(CO)_2(PEt_3)_3$ are accompanied by an additional weak band which is assigned to the asymmetric stretch of a bis axial isomer. The PEt_3 example of this molecule thus contains detectable populations of *two* isomers in pentane solvent, although only one is found in the crystalline solid. For $Ru(CO)_2$(P-*i*-$Pr_2Me)_3$, the single strong absorption at 1867 cm^{-1} in pentane (see Supporting Information) assigned to the *trans* isomer is accompanied by a significant shoulder at *ca.* 1850 cm^{-1} (whose energy and intensity exclude its assignment as that of a ^{13}CO isotopomer) which could be assigned to the asymmetric stretch of a bis equatorial isomer; the symmetric stretch of this isomer (expected about 60 cm^{-1} higher) is calculated[4] to have an intensity only 9% of the observed band[10] and thus could remain

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[‖] Dedicated to Walter Siebert on the occasion of his 60th birthday.

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(9) In the third isomer, the CO ligands are found to be equatorial and axial. Its energy is close to that of the bis equatorial isomer. This finding illustrates the fact that CO can equally well occupy the equatorial or axial site of a TBP. This isomer will not be considered further since the mutual proximity of the phosphine ligands in this isomer may disqualify it as a potential minimum with the bulky phosphines in the actual complexes. This point is under study.

(10) This value was calculated by assuming a C−Ru−C angle of 147°, which came from the results of X-ray structure determination of $Ru(CO)_2$(P-*i*-$Pr_2Me)_3$.

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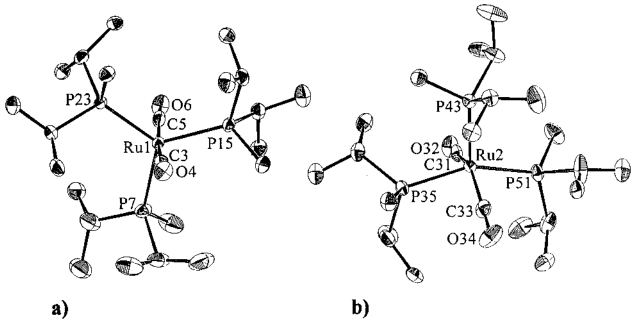


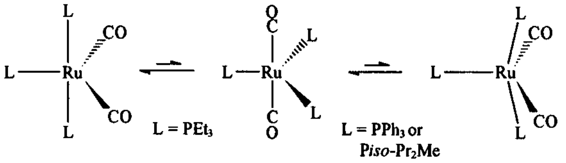
Figure 2. ORTEP drawings of the non-hydrogen atoms of two independent molecules in solid $Ru(CO)_2(P\text{-}i\text{-}Pr_2Me)_3$.

undetected. The lower frequency in the bis equatorial isomer is consistent with the better back-donation expected for the bent OC−Ru−CO unit. In the more polar solvents THF and EtOH, the relative intensity of the lower energy band progressively increases, consistent with an increasing mole fraction of the more polar bis equatorial isomer relative to the nonpolar bis axial (see Supporting Information). Our reexamination of the IR spectrum of $Ru(CO)_2(PPh_3)_3$[5] in C_6D_6 shows an unreported (weaker) band at 1856 cm^{-1} which we also assign to a co-existing bis equatorial isomer.

$Ru(CO)_2(P\text{-}i\text{-}Pr_2Me)_3$ is a solid with low melting point, which requires low temperatures for solid-state structure determination. The X-ray structure at −173 °C reveals[11] a unit cell containing two independent molecules (Figure 2). One of these (Figure 2a) is a nearly ideal bis axial isomer based on a trigonal bipyramid. It is thus very similar to the calculated isomer **I**. The RuC_2P_3 substructure has nearly perfect C_{3v} symmetry, with angles deviating from 90° or 120° by less than 8°. The other independent molecule (Figure 2b) has an RuC_2P_3 substructure of C_{2v} symmetry. This second isomer shows how interphosphine repulsions distort the calculated isomer **II**: the two *cis* P−Ru−P angles enlarge to 105.31(4) and 100.30(4)°, while the angle C−Ru−C enlarges to 146.68(18)°. The fact that only one set of NMR signals is seen even at −93 °C in toluene-d_8 for the isomeric mixture is evidence for the facile fluxionality expected for pentacoordination (Scheme 1).

While the d^8 species $Ni(CN)_5^{3-}$ also shows both trigonal-bipyramidal *and* square-pyramidal forms in its solid $Cr(en)_3^{3+}$ salt, this has been attributed to solid-state packing effects.[12] Two other cases of coexistence of isomers for other d^8 species in solution have been reported.[13]

Scheme 1



The structure of the distorted bis equatorial isomer of $Ru(CO)_2(P\text{-}i\text{-}Pr_2Me)_3$ is strongly related to that of the 16-electron, nonplanar *four*-coordinate $Ru(CO)_2(P\text{-}t\text{-}Bu_2Me)_2$,[14] which has been described as a trigonal bipyramid with one equatorial position unoccupied. The remarkable thing about that structure is that there was so little relaxation (i.e., modification) of an ideal TBP structure upon removal of one equatorial ligand. With the structure of bis-equatorial-$Ru(CO)_2(P\text{-}i\text{-}Pr_2Me)_3$ now available for comparison, we can see that the small relaxation involves bending of the (original two axial) phosphines away from the incoming ligand (by about 20° for each phosphorus), and modest (7°) angular movement (and linearization of angle Ru−C−O) by each CO. The newly arrived (i.e., equatorial) phosphine in bis-equatorial-$Ru(CO)_2(P\text{-}i\text{-}Pr_2Me)_3$ has a slightly (∼0.02 Å) longer Ru−P distance than the axial phosphines, symptomatic of weaker metal-equatorial ligand bonds. However, attempts to synthesize *four*-coordinate $Ru(CO)_2(P\text{-}i\text{-}Pr_2Me)_2$ by Mg reduction of *cis,cis,trans*-$RuCl_2(CO)_2(P\text{-}i\text{-}Pr_2Me)_2$ in THF without addition of P-*i*-Pr_2Me yield $Ru(CO)_2(P\text{-}i\text{-}Pr_2Me)_3$, along with uncharacterized products of decomposition. Apparently, the steric protection against phosphine addition to the unsaturated $Ru(CO)_2(PR_2Me)_2$ is successful when R = *t*-Bu but not sufficient when R = *i*-Pr.

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Supporting Information Available: Tables of full crystallographic details, positional parameters, and bond lengths and angles for $Ru(CO)_2(P\text{-}i\text{-}Pr_2Me)_3$ and figure showing IR spectra for $Ru(CO)_2(P\text{-}i\text{-}Pr_2Me)_3$ in different solvents (5 pages). Ordering information is given on any current masthead page.

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(11) Cell constants (−173 °C): $a = 16.930(2)$ Å, $b = 17.932(2)$ Å, $c = 9.540(1)$ Å, $\alpha = 93.27(1)°$, $\beta = 91.90(1)°$, $\gamma = 102.04(1)°$ with $Z = 4$ in space group $P\bar{1}$. $R(F) = 0.0345$ for 6584 observations with $F > 3\sigma(F)$.

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