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Hindered rotation about single bonds in $RuHX(CO)(P^tBu_2Me)_2$ and $IrHCl_2(P^tBu_2Me)_2$ ☆

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Abstract

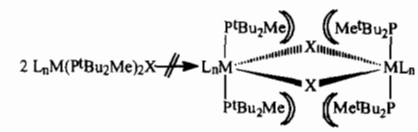
$Ru[C(O)Me]I(CO)L_2$ ($L = P^tBu_2Me$) shows ^1H and ^{31}P NMR evidence for existence of two conformers (distinguished by their rotational conformation about the Ru–P bonds) which show (at −80 °C) (a) no symmetry and (b) mirror symmetry (defined by the Ru[C(O)Me]I(CO) plane). The same is true of $RuH(Cl)(CO)L_2$. $Ru(Me)I(CO)L_2$ shows (^1H and ^{31}P evidence) two conformers, *each* mirror symmetric, with a lower interconversion barrier than in the acetyl analog. The molecules $RuCl(Ph)(CO)L_2$ and $RuH(Ph)(CO)_2L_2$ exhibit slow (^1H and ^{13}C NMR time scales) rotation about the Ru–C(*ipso*) bond at 23 °C. Already at 23 °C, IrL_2Cl_2H shows ^1H and ^{31}P NMR evidence for two equally abundant (mirror symmetric) conformers due to hindered rotation about Ir–P bonds.

Keywords: Hindered rotation; Ruthenium complexes; Iridium complexes; Hydride complexes; Halide complexes; Carbonyl complexes; Phosphine complexes

1. Introduction

An exceptionally thorough and systematic study is available of the kinetics and thermodynamics of conformers of four-coordinate, planar $MX_2(P^tBu_2Me)_2$ and $M'(CO)X(P^tBu_2Me)_2$ molecules (M = Pd, Pt; M′ = Rh, Ir; X = halide) [1,2]. This work has revealed that, while this bulky phosphine shows rotation about the M–P bond which is fast on the NMR time scale near room temperature (e.g. half-life of 10^{-2} s at 310 K for $PtCl_2(P^tBu_2Me)_2$), rotation can be very slow at low temperature (half-life of 22 years at 160 K). That low-temperature work has revealed that, in the favored conformer, the P–CH_3 bond eclipses the M–X bonds, so that all ^{t}Bu groups avoid eclipsing M–X bonds and thus project to the 'open' sides of the coordination plane [3].

No such comparable study exists for five-coordinate molecules, although these would be expected to experience even greater steric interactions than those in the above four-coordinate molecules. We have been studying the reactivity of five-coordinate, 'operationally-unsaturated' molecules of the formula $IrH_nCl_{3-n}(P^tBu_2Me)_2$ ($n = 1,2$) [4–6] and $RuHX(CO)(P^tBu_2Me)_2$ [7–10]. Our choice of bulky phosphine was motivated by a desire to avoid 'quenching' of unsaturation by halide bridging (Eq. (1)).



(1)

In the course of this work, we have already reported several instances of broad $^{31}P\{^1H\}$ NMR signals at or near 25 °C, or unexpected spectral complexity at lower temperatures [1]. For example, the $^{31}P\{^1H\}$ NMR spectrum of **1** ($L = P^tBu_2Me$) shows only a broad signal at 25 °C, and, at −40 °C, an AB spectrum ($J_{AB} = 273$ Hz) is consistent with the existence of a single conformer in which the *trans* phosphines are inequivalent due to hindered rotation about the Ru–P bonds [10]. Resistance

☆ Dedicated, with appropriate affection, to the evangelist of routine crystallography (see *J. Am. Chem. Soc.*, *95* (1973) 3798), to recall what can still be learned (only) via 'sporting methods'.

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[1] We have also reported [7] that pyridine coordinated to $RuH(OCH_2CF_3)CO(P^tBu_2Me)_2$ (i.e. a *six*-coordinate molecule) results in an AB $^{31}P\{^1H\}$ NMR pattern ($J_{AB} = 360$ Hz) at −85 °C *and* that pyridine does not rotate rapidly about its Ru–N bond (five ^1H NMR chemical shifts are observed at −60 °C).

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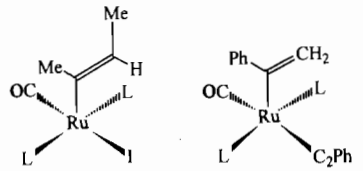
to rotation about these single bonds is attributed to the bulky neighboring halide and α-methyl vinyl



1 2

groups. The branched vinyl compound **2** likewise has a broad $^{31}P\{^1H\}$ NMR signal at 25 °C. At −40 °C, this $^{31}P\{^1H\}$ NMR spectrum decoalesces into two signals.

We report here several more systematic studies of other examples of conformational 'locking' of phosphine and other substituents in the five-coordinate species $Ir(P^tBu_2Me)_2HCl_2$ and $RuH(X)CO(P^tBu_2Me)_2$. Particularly because these show spectral evidence for hindered rotation at and near 25 °C, their first observation causes confusion as to the origin of broad NMR signals. The results reported here also serve to emphasize how an effort to prevent dimerization (Eq. (1)) has the consequence of creating monomers which are very highly sterically congested. We have already commented briefly on how this places severe constraints on the size of donor molecules which are able to serve as ligands, e.g. the weak binding of ethylene to $Cp^*Ru(P^iPr_2Ph)X$ where $X=OCH_2CF_3$, Cl and I [11].

2. Experimental

2.1. General

All manipulations were carried out using standard Schlenk and glovebox techniques under prepurified argon. Bulk solvents (pentane, toluene) were dried and deoxygenated over sodium or potassium benzophenone and subjected to three freeze–pump–thaw cycles prior to use. Benzene-d_6 and toluene-d_8 were dried over sodium metal and vacuum-distilled prior to use. PhLi was purchased from Aldrich [12]. ^1H and ^{13}C (referenced via residual solvent impurity), and $^{31}P\{^1H\}$ (referenced to 85% H_3PO_4) NMR spectra were recorded on Nicolet NT-360 or Bruker AM500 spectrometers. IR spectra were recorded in C_6D_6 (NaCl cavity cell, 0.1 mm path length) on a Nicolet 510 FT-IR spectrometer.

2.2. $Ir(P^tBu_2Me)_2Cl_2H$

400 mg (0.45 mmol) $[Ir(COE)_2Cl]_2$ was dissolved in 10 ml of toluene and a solution of 307 mg (1.02 mmol) P^tBu_2Me in 3 ml of toluene was added. After 5 min, 0.87 ml of a 1.03 M solution of HCl in Et_2O was added. Upon addition, a deep purple solid precipitated. The solvent was removed in vacuo leaving a mixture of purple and pale yellow solids. The mixture was then refluxed for 5 h in 10 ml of isopropanol. The solution was allowed to cool to room temperature and after 5 days, the product was isolated in the form of deep purple crystals. Renewed refluxing of the yellow mother liquor changed its color to purple again and a second crop of crystals could be isolated. Total yield 462 mg (0.79 mmol, 89%).

2.3. $RuHPh(CO)[P(^tBu)_2Me]_2$

A Schlenk flask was charged with $RuHCl(CO)[P(^tBu)_2Me]_2$ (0.53 g, 1.1 mmol) and pentane (40 ml) to give an orange heterogeneous mixture. The mixture was cooled to −15 °C with a dry ice/$HOCH_2CH_2OH$ slush bath and 1.4 M PhLi (0.80 ml of a solution in cyclohexane/Et_2O, 1.1 mmol) was added via syringe. The mixture quickly became darker orange and less heterogeneous. After stirring at −15 °C for 1 h, the volatiles were removed. The resulting orange residue was extracted with pentane (2×15 ml), filtered, and concentrated at −15 °C. Cooling to −75 °C provided 0.24 g of orange microcrystals, isolated by filtration. The mother liquor was concentrated, and a second crop of orange microcrystals was obtained by cooling to −75 °C. The total yield was 0.33 g (0.63 mmol, 57%). ^1H NMR (toluene-d_8, −70 °C): δ −28.60 (t, J(PH) = 19.5 Hz, 1H, Ru*H*), 0.61 (br s, 6H, PCH_3), 1.07 (br s, 36H, PCCH_3), 7.22 (m, 1H, *p*-C_6H_5), 7.38 (m, 2H, *m*-C_6H_5), 7.78 (d, J(HH) = 6.1 Hz, 2H, *o*-C_6H_5). ^1H NMR (benzene-d_6, 23 °C): δ 0.65 (t, J(PH) = 2.5 Hz, 6H, PCH_3), 1.11 (t, J(PH) = 6.1 Hz, 18H, PCCH_3), 1.15 (t, J(PH) = 6.1 Hz, 18H, PCCH_3). $^{13}C\{^1H\}$ NMR (toluene-d_8, −70 °C): δ 7.02 (br s, PCH_3), 28.61 (br s, PCCH_3), 34.93 (t, J(PC) = 9.1 Hz, PCCH_3), 36.33 (t, J(PC) = 7.3 Hz, PCCH_3), 121.4, 133.2, 142.8 (all s, *p*, *m*, *o*-C_6H_5), 187.2 (t, J(PC) = 14.5 Hz, *ipso*-C_6H_6), 207.5 (t, J(PC) = 10.9 Hz, *C*O). $^{31}P\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 57.4. IR (cm^{-1}): ν(CO) = 1896.

2.4. $RuHPh(CO)_2[P(^tBu)_2Me]_2$

A Schlenk flask was charged with $RuHPh(CO)[P(^tBu)_2Me]_2$ (0.035 g, 0.066 mmol) and benzene (10 ml) was added to create an orange solution. The solution was degassed, and CO (650 torr) was added. The solution was allowed to warm to room temperature, and was stirred for 3 h. The color changed to pale yellow within the first half hour. The volatiles from the pale yellow solution were removed to yield a pale yellow solid. ^1H NMR (benzene-d_6, 23 °C): δ −5.80 (t, J(PH) = 22.4 Hz, 1H, Ru*H*), 0.72 (t, J(PH) = 2.9 Hz, 6H, PCH_3), 1.19 (t, J(PH) = 6.1 Hz, 18H, PCCH_3), 1.21 (t, J(PH) = 6.1 Hz, 18H, PCCH_3), 7.04 (m, 2H, C_6H_5), 7.13 (m, 1H, C_6H_5), 7.91 (t, J = 3.2 Hz, 1H, C_6H_5), 8.02 (d, J = 7.6 Hz, 1H, C_6H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 8.15 (t, J(PC) = 11.9 Hz, PCH_3), 29.76 (s, PCCH_3), 30.06

(s, PCCH$_3$), 36.43 (t, J(PC) = 10.6 Hz, PCCH$_3$), 36.89 (t, J(PC) = 8.2 Hz, PCCH$_3$), 121.7, 126.1, 127.1 (all s, *p*, *m*-C_6H_5), 145.4, 150.5 (both s, *o*-C_6H_5), 165.1 (t, J(PC) = 13.6 Hz, *ipso*-C_6H_5), 204.4 (t, J(PC) = 11.3 Hz, RuCO), 205.9 (t, J(PC) = 6.5 Hz, RuCO). $^{31}P\{^1H\}$ NMR (benzene-d$_6$, 23 °C): δ 60.3. IR (cm^{-1}): ν(CO) = 1987, 1921. *Anal.* Calc. for $C_{26}H_{48}O_2P_2Ru_2$: C, 56.20; H, 8.71. Found: C, 56.20; H, 8.88%.

2.5. Ru(Me)I(CO)L$_2$ from RuH(Ph)(CO)L$_2$ and MeI

A Schlenk flask was charged with RuHCl(CO)L$_2$ (0.26 g, 0.53 mmol). Pentane (30 ml) was added, and the heterogeneous orange mixture was cooled to −10 °C. PhLi (0.4 ml, 0.56 mmol) was added via syringe, and the now darker orange heterogeneous mixture was stirred for 1 h. The volatiles were removed at low temperature, and the residue (RuHPh(CO)L$_2$) was extracted with benzene (20 ml) at room temperature.

After the insolubles were removed by filtration, MeI (0.035 ml, 0.56 mmol) was added via syringe. Within minutes, the solution became red–orange. After stirring for 2 h, the volatiles were removed, and the red–orange residue was extracted with pentane (2×15 ml). After filtering away a small amount of insoluble material, the solution was concentrated and cooled, yielding two crops of light red solid totalling 0.19 g (0.32 mmol, 60%). ^1H NMR (C_6D_6, 23 °C): δ 1.21 (br t, J(PH) = 6.1 Hz), 1.34 (br m, RuMe and ^{t}Bu). $^{13}C\{^1H\}$ NMR (benzene-d$_6$: 25 °C): δ −9.3 (br s, RuCH$_3$), 7.2 (br s, RuPCH$_3$), 30.28 (br s, RuPCCH$_3$), 30.51 (br s, RuPCCH$_3$), 36.05 (t, J(PC) = 8.2 Hz, RuPCCH$_3$), 37.86 (t, J(PC) = 7.6 Hz, RuPCCH$_3$), 202.0 (t, J(PC) = 13.9 Hz, RuCO). $^{31}P\{^1H\}$ NMR (C_6D_6, 23 °C): δ 30.9 (br). IR (C_6D_6): ν(CO) = 1900 cm^{-1}.

2.6. Ru(COMe)I(CO)L$_2$

A Schlenk flask was charged with Ru(Me)I(CO)L$_2$ (0.065 g, 0.11 mmol). Toluene (15 ml) was added, and the light red solution was freeze–pump–thaw degassed three times. CO (30 Torr, 0.11 mmol) was added, and the frozen solution warmed to room temperature. After several minutes, the solution became bright yellow. After stirring for 3 h, the volatiles were removed. Crystallization of the yellow residue from pentane provided two crops of bright yellow microcrystals totalling 0.55 g (0.089 mmol, 81%). ^1H NMR (C_6D_6, 23 °C): δ 1.17 (t, J(PH) = 6.3 Hz, 36H, PCCH$_3$), 1.82 (br s, 6H, PCH$_3$), 2.96 (s, 3H, RuCOCH$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 23 °C): δ 38.6 (br). IR (C_6D_6 solution): ν(CO) = 1929, 1630 cm^{-1}.

2.7. Ru(CO)L$_2$(Ph)Cl

A Schlenk flask was charged with Ru(CO)L$_2$(Ph)H (0.185 g, 0.35 mmol) and *N*-chlorosuccinimide (0.060 g, 0.45 mmol), and benzene (20 ml) was added to give an orange solution. While stirring for 6 h, the solution became pale orange. The volatiles were removed, and the pale orange residue was extracted with pentane (2×15 ml). The insolubles were removed by filtration, and the pale orange solution was concentrated to 5 ml, with formation of a precipitate. The solution was again filtered and then further concentrated to about 2 ml. Cooling the solution to −40 °C deposited a dark orange precipitate, which became pale orange upon drying and provided 0.10 g of crude product (0.18 mmol, 51%). ^1H NMR (benzene-d$_6$, 23 °C): δ 1.03 (overlapping t, J(PH) = 6.5 Hz, 36H, PCCH$_3$), 1.44 (t, J(PH) = 2.5 Hz, 6H, PCH$_3$), 6.71 (m, 2H, *m*-C_6H_5), 6.79 (m, 1H, *p*-C_6H_5), 7.33 (d, J(HH) = 7.6 Hz, 1H, *o*-C_6H_5), 8.36 (d, J(HH) = 7.2 Hz, 1H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR (benzene-d$_6$, 23 °C): δ 4.45 (t, J(PC) = 9.8 Hz, PCH$_3$), 29.57 (s, PCCH$_3$), 30.32 (s, PCCH$_3$), 36.16 (t, J(PC) = 8.6 Hz, PCCH$_3$), 37.25 (t, J(PC) = 8.2 Hz, PCCH$_3$), 121.6, 125.7, 127.5 (all s, *m*, *p*-C_6H_5), 139.4, 141.4 (both s, *o*-C_6H_5), 155.7 (t, J(PC) = 9.8 Hz, i-C_6H_5), 205.1 (t, J(PC) = 13.9 Hz, RuCO). $^{31}P\{^1H\}$ NMR (benzene-d$_6$, 23 °C); δ 34.1. IR (benzene-d$_6$ solution): ν(CO) = 1902 cm^{-1}.

3. Results and discussion

3.1. Five-coordinate ruthenium complexes containing two P^{t}Bu$_2$Me ligands

NMR spectra of the five-coordinate complex Ru[C(O)Me]I(CO)L$_2$ in toluene-d$_8$ clearly show evidence of steric congestion at 25 °C. The $^{31}P\{^1H\}$ NMR spectrum is one very broad signal at 25 °C, which begins to decoalesce by 0 °C and, at −80 °C (Fig. 1) is fully resolved into an M_2 singlet (37.7 ppm) and an AB quartet (δ_A and δ_B are 38.3 and 33.6 ppm and J_{AB}, 236 Hz, indicates mutually *trans* phosphines). It is reasonable that the acetyl group lies in the Ru–I–CO plane, and thus the AB and M_2 species detected by ^{31}P NMR will be an asymmetric and a mirror-symmetric conformer due to hindered rotation about the Ru–P bonds. These observations are confirmed by ^1H NMR data, which show only one (averaged) set of resonances for C(O)Me, one for PMe and one for P^{t}Bu protons at 25 °C. Two acetyl methyl signals begin to become evident by −20 °C, and are well resolved at −40 and −80 °C (where their chemical shifts are 3.09 and 2.90 ppm). The PMe and P^{t}Bu signals also decoalesce upon cooling, with (at −40 °C) one PMe and one P^{t}Bu set for the symmetric isomer, and two PMe and four P^{t}Bu signals for the asymmetric isomer.

For Ru(Me)(I)(CO)L$_2$, there is evidence for hindered interconversion among two conformers, but with a reduced activation barrier, consistent with Me being smaller than C(O)Me. Thus, the $^{31}P\{^1H\}$ NMR spectrum

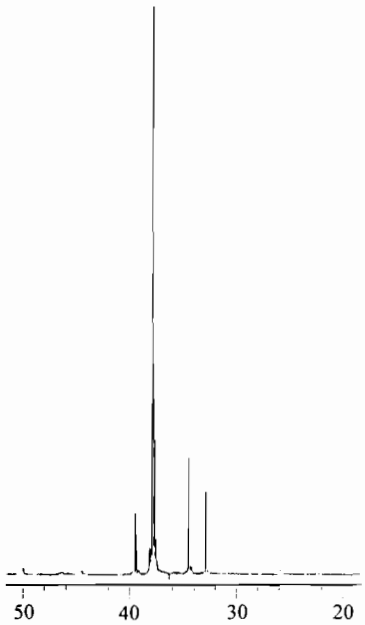
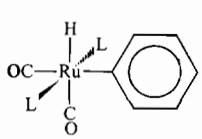


Fig. 1. 146 MHz $^{31}P\{^1H\}$ NMR spectrum of Ru[C(O)Me](I)(CO)(P^tBu_2Me)$_2$ at −80 °C in toluene-d_8.

in toluene-d_8, is one slightly broad line at 25 °C, and decoalesces into two *singlets* (30.3 and 30.1 ppm, intensity 3:1) at −60 °C. Each frozen conformer thus has mirror symmetry. The $^{13}C\{^1H\}$ NMR spectrum at 25 °C shows one *broad* Ru–Me resonance and one broad P–Me resonance [2] consistent with interconversion between conformers at a rate comparable to the NMR time scale. The 25 °C ^1H NMR spectrum is particularly disappointing, with only a P^{t}Bu triplet and a broad resonance (with a shoulder) at 1.33 ppm, assigned to unresolved PMe and RuMe. At −60 °C, one sees a total of six methyl signals which agrees with what would be expected for two symmetric Ru(Me)(I)(CO)L_2 conformers [3]. These six resonances come in pairs (i.e. RuMe, PMe and P^{t}Bu) of intensity 1:3, which agrees with the conformer intensities observed by ^{31}P NMR at this temperature. The broad singlet resonances assigned to the Ru–Me groups have −60 °C chemical shifts of 1.94 (intensity 1) and 1.15 (intensity 3).

Although there is rapid rotation about the Ru–C bond in RuH(Ph)(CO)L_2 even at −70 °C, this molecule adds CO to give dicarbonyl **3**. This six-coordinate molecule shows a total of six aryl ^{13}C chemical shifts and five aryl ^1H NMR chemical shifts, all at 23 °C. It is certain that this arises from restricted rotation within a single conformer (rather than from co-existence of several conformers) because there is only one hydride NMR signal, one ^{31}P NMR signal and only two ^{13}CO signals [4,5].



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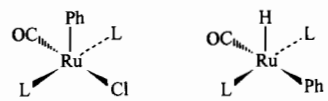
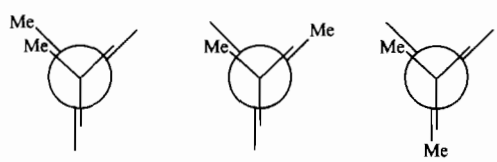
While addition of a CO ligand to RuH(Ph)(CO)L_2 slows phenyl rotation, even the five-coordinate molecule where chloride replaces hydride can accomplish this. Thus, RuCl(Ph)(CO)L_2 shows six aryl ^{13}C chemical shifts and five aryl ^1H NMR chemical shifts, all at 23 °C. There is only one $^{31}P\{^1H\}$ NMR signal at 23 °C. Since a strong σ-donor ligand is generally found at an apical site of a square pyramid and halide is normally *trans* to CO (for best halide-to-CO backdonation through Ru), the anticipated structure is **4**, and thus phenyl in this molecule (unlike **5**) is *cis* to *four* other ligands. This will raise the barrier for phenyl rotation about the Ru–C bond and rationalize why phenyl rotation is rapid in **5**.



4 **5**

Even RuHCl(CO)L_2 shows low-temperature evidence for crowding [9]. At −85 °C in toluene, the $^{31}P\{^1H\}$ NMR spectrum consists of an AB pattern (with J_{AB} = 265 Hz, indicating that the inequivalent phosphines are *trans*) and an M_2 pattern (which requires a molecule with a mirror plane of symmetry). These results indicate steric hindrance sufficient that conformers interconvert only slowly at −85 °C. The hindered rotation is presumably around the Ru/P single bonds. Drawing Newman projections for the two phosphorus rotors, **6** and either **7** or **8**, will account for the observations. In summary, even when the three ligands X, Y and Z in Ru(X)(Y)(Z)(P^tBu_2Me)$_2$ are relatively small, there is low-temperature NMR evidence for slowly interconverting 'conformational isomers' due to the bulk of the two P^{t}Bu$_2$Me ligands.



6(M$_2$) **7(AB)** **8(AB)**

[2] The $PCCH_3$ resonances are also broadened, but not as much as the PMe signal.

[3] It has not been possible to resolve the expected two ^{t}Bu signals for each conformer.

[4] *Six*-coordinate Ru(Ph)(X)(CO)$_2$(PMe_2Ph)$_2$ compounds, which have been shown by X-ray diffraction to have the phenyl plane perpendicular to the P–Ru–P line, show separate *ortho* carbon resonances at 25 °C. Given the smaller size of this phosphine, this conformational preference was attributed to preferential Ru → π^*(Ph) backdonation; see Ref. [13].

[5] Previous examples of hindered M-phenyl rotation have been reported in Ref. [14].

3.2. Synthesis of $Ir(P^tBu_2Me)_2Cl_2H$

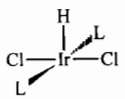
$Ir(P^tBu_2Me)_2Cl_2H$ (**9**) [15] was prepared analogous to $Ir(P^iPr_3)_2Cl_2H$ as reported by Werner et al. [16]. $[Ir(COE)_2Cl]_2$ is reacted with four equivalents of P^tBu_2Me (Eq. (2)) to give the intermediate 'IrL_2Cl' which oxidatively adds HCl to give the product. The

$$\tfrac{1}{2}[Ir(COE)_2Cl]_2 \xrightarrow[-2COE]{+2P^tBu_2Me} \text{'}[Ir(P^tBu_2Me)_2Cl]\text{'} \xrightarrow{+HCl} \underset{\mathbf{9}}{Ir(P^tBu_2Me)_2Cl_2H} \quad (2)$$

mechanism of this reaction, however, seems to be more complex because other species are visible in the ^{31}P NMR spectra of the crude product. These products are the dimeric species described by Shaw and coworkers [17].

3.3. Dynamic NMR studies

The structure of IrL_2HCl_2 (**9**) is square-pyramidal [18,5]. At 25 °C, the 146 MHz $^{31}P\{^1H\}$ NMR spectrum in toluene-d_8 shows two broad lines of equal intensity.



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These signals coalesce at higher temperatures (Fig. 2), showing that the two signals at 25 °C are due to species with the same chemical formula. At −50 °C, two sharp signals of approximately equal intensity are observed. In the hydride-coupled (−49 ppm, see below) spectrum at −50 °C, each ^{31}P NMR line becomes a doublet due to coupling to one hydride. Since there is no P–P coupling, it must be concluded that these spectra are due to two *different* species (i.e. conformers), each of which has two equivalent phosphines (i.e. each has C_2 or mirror symmetry).

The hydride region of the ^1H NMR spectrum (500 MHz, toluene-d_8, Fig. 3) confirms the conclusion of two distinct species. Although the hydride signal near −49 ppm is an apparent triplet at 23 °C (with slightly broadened lines), it becomes clear at 0 °C and below that this is really two overlapping triplets. The spin system is thus two AX_2 patterns rather than one AX_2 (or an AXZ, due to inequivalent phosphines). While the ^1H NMR signals of the PMe and P^tBu groups are broadened and uninformative at 23 °C (Fig. 4), at lower temperatures they resolve into two approximately equally populated PMe virtual triplets and four P^tBu virtual triplets. This pattern is alo consistent with two two-fold symmetric or mirror symmetric conformers. The *four* ^{t}Bu chemical shifts indicate that the ground state structure of each conformer lacks a mirror plane

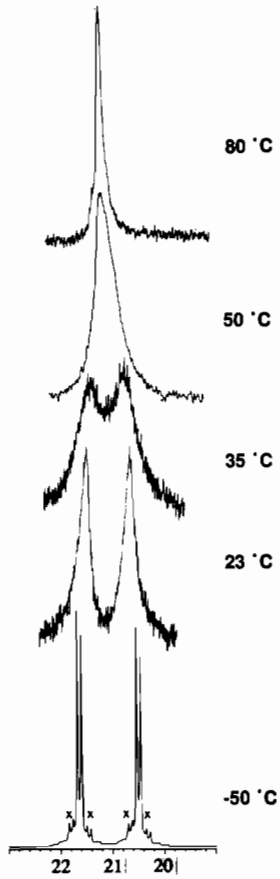


Fig. 2. Variable-temperature 146 MHz $^{31}P\{^1H\}$ NMR spectra of $IrHCl_2(P^tBu_2Me)_2$ in toluene-d_8. The −50 °C spectrum is selectively hydride-coupled. 'X' denotes spinning sidebands.

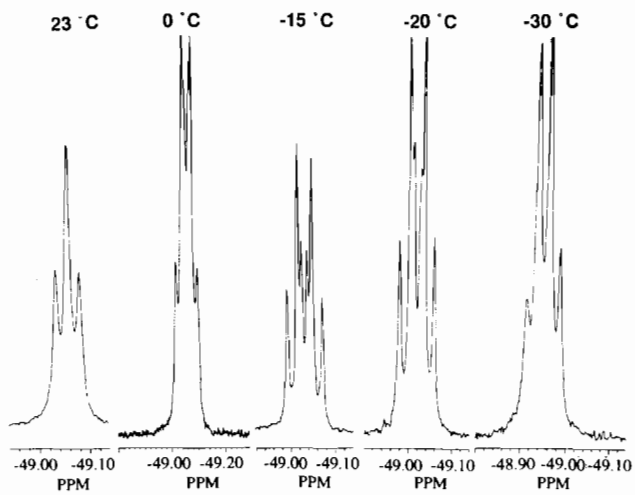


Fig. 3. Variable-temperature 500 MHz ^1H NMR signals of the hydride nuclei of $IrHCl_2(P^tBu_2Me)_2$ in toluene-d_8.

of symmetry relating the two ^{t}Bu groups on one phosphorus.

It has been shown that the mutual interactions between two *trans* phosphines are small, and thus the rotational conformation about an M–P bond is controlled by *cis* interactions between phosphine and (in

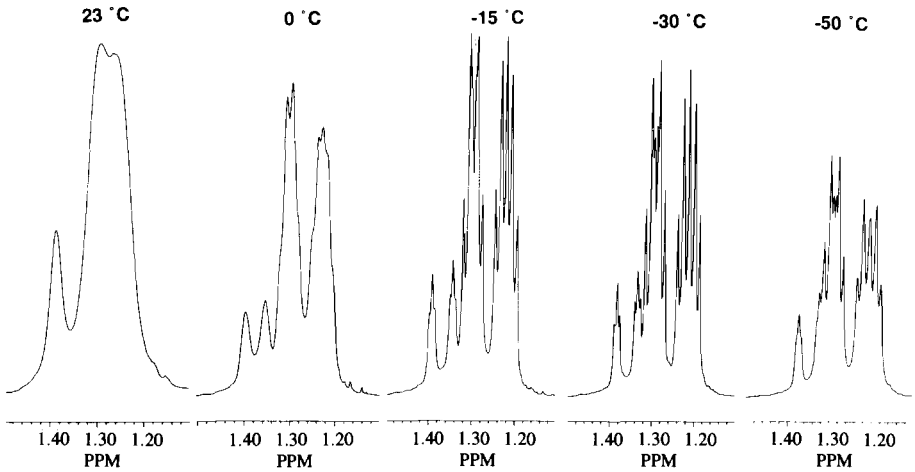
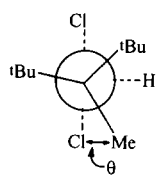


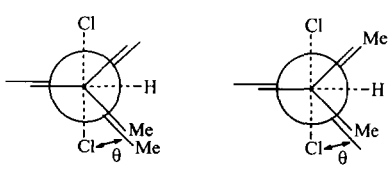
Fig. 4. Variable-temperature 500 MHz ^{1}H NMR signals of the methyl and ^{t}Bu protons of $IrHCl_2(P^tBu_2Me)_2$.

our case) the groups in the $IrHCl_2$ or Ru(CO)XY plane. In $M(CO)ClL_2$ (M = Rh and Ir) and in $M'Cl_2L_2$ (M' = Pd and Pt), the favored conformer (also that seen in the solid state) has the methyl group eclipsing one *cis* ligand. This will undoubtedly be modified somewhat for $IrHCl_2L_2$ (i.e. $\theta \neq 0$ in **10**, which shows only the relationship of the $IrCl_2H$ rotor to one P^tBu_2Me rotor)



10

in order to decrease ^{t}Bu/hydride repulsions. However, there remain two basic ways to arrange the (eclipsed) phosphine substituents (**11** and **12**, where the ^{t}Bu groups have been omitted for simplicity), and these are sufficient to account for the spectral observations. The expected comparable magnitude of the *cis* interactions in **11** and **12** is consistent with the comparable conformer populations derived from the intensity of all observed NMR signals [6].

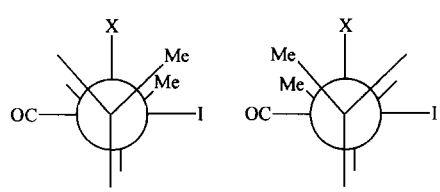


11(σ) **12**(C_2)

[6] It should be noted that **6** and **11** are analogs. Likewise, **7** and **8** are analogs of **12**. The main difference is that the Ru(X)(Y)(Z) unit does not permit a C_2 axis of symmetry while the $IrHCl_2$ unit does. The conformational analysis for these two metals is thus more similar than different, and the interpretation in terms of conformers is strengthened by its ability to account for the spectral behavior of both metals.

4. Conclusions

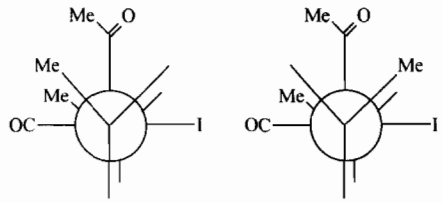
It is clear from the multiple examples reported here that five- and six-coordinate molecules [7] containing two mutually *trans* P^tBu_2Me ligands have considerable steric impact. A planar co-ligand like pyridine or phenyl experiences hindered rotation about the bond between the metal and that ligand. NMR phenomena reveal hindered rotation about the M–P bond even at 23 °C. The most stable conformers sometimes have equivalent phosphines (i.e. σ or C_2 symmetry), but other times one has no symmetry (i.e. inequivalent phosphines). The controlling factors here will be the interactions of the phosphine substituents with the *cis*-substituents X, Y and Z in $M(X)(Y)(Z)(P^tBu_2Me)_2$. These have already been shown to be difficult to quantitate even in four-coordinate $M(X)(Y)(P^tBu_2Me)_2$ species. One provocative distinction warrants brief discussion, however. The compounds $RuXI(CO)L_2$ show two M_2 patterns when $X = CH_3$ but one M_2 and one AB pattern when $X = C(O)CH_3$. This can be understood as follows.



13 **14**

While conformers **13** and **14** account for the two M_2 $^{31}P\{^1H\}$ NMR patterns when $X = CH_3$, steric interactions between the group $C(O)CH_3$ and the ^{t}Bu groups will disfavor conformer **15**, and permit **16** (an AB spin system) to attain detectable population.

[7] Phenyl rotation can be slowed, with observation of two rotamers, in $CpRh(H)(PMe_3)(o\text{-}C_6FH_4)$ [19]. When there are *four* phosphine ligands (e.g. $M(PR_3)_4X_2$), restricted rotation around M–P bonds becomes evident for even smaller phosphines [20].



15 16

Low-temperature NMR studies of the reactivity of this class of molecules must recognize this complexity in order to avoid erroneous conclusions about multiple 'isomeric' products.

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