Effect of Lewis Acidity on the Synthesis of RuHCl(CO)(phosphine)$_2$: Subtle Influence of Steric and Electronic Effects among P^{i}Pr$_3$, P^{i}Pr$_2$(3,5-(CF$_3$)$_2$C$_6$H$_3$), and P^{i}Pr$_2$Me

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Received May 9, 2000

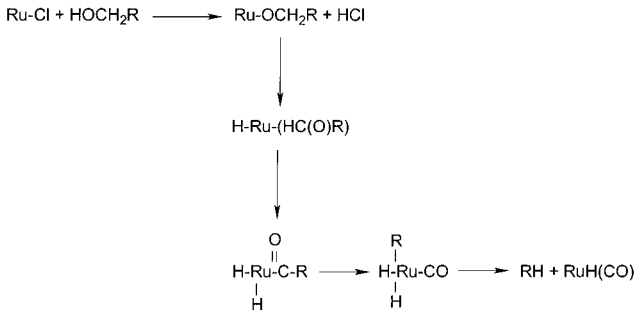
To evaluate the influence of steric, electronic, and synthetic factors, the synthesis of RuHCl(CO)[P^{i}Pr$_2$(3,5-(CF$_3$)$_2$C$_6$H$_3$)]$_2$ was carried out, and its Lewis acidity toward Cl$^-$ was compared to that of RuHCl(CO)(P^{i}Pr$_3$)$_2$. In this synthesis, Na$_2$CO$_3$ was shown to be a more effective base than NEt$_3$, because Na$^+$ can better mask the nucleophilicity of the potential ligand Cl$^-$. An X-ray structure determination of the hydride-free species RuCl$_2$(CO)(P^{i}Pr$_2$Me)$_2$ shows it to be a dimer, and this solid-state structure persists in solution, but as several different isomers. The synthesis of RuHCl(CO)(P^{i}Pr$_2$Me)$_3$ shows that three of this smaller phosphine can crowd around Ru, but dynamic NMR spectra show one phosphine to be weakly bound. The rate of reaction of Me$_3$SiC≡CH with this molecule is suppressed by added free P^{i}Pr$_2$Me, indicating phosphine dissociation to be a mechanistic component.

Introduction

A large number of Ru(II) monocarbonyl complexes are known,[1] and they fall into several different classes: five- and six-coordinate, monomeric RuXCl(CO)(PR$_3$)$_{2\ or\ 3}$, where X = H or Cl, and also dimeric [RuCl$_2$(CO)(PR$_3$)$_2$]$_2$. While a broad range of phosphines have been surveyed, there are no general principles allowing prediction of whether bis- or tris-phosphine species will be produced. Certainly, some of the products are formed under kinetic control, so no conclusion is possible about how many phosphines *can* coordinate to one Ru. It is probable, however, that any monomer/dimer equilibrium is achieved, so thermodynamic conclusions are possible on this issue. For example, RuCl$_2$(CO)(P^{t}Bu$_2$Me$_2$)$_2$[2] and RuCl$_2$(CO)(P^{i}Pr$_3$)$_2$[3] are monomers, but the PMe$_2$Ph analogue is a dimer,[4] in a case probably attributable to steric effects. More subtle steric changes, and the influence of electronic factors, are beyond our current ability to predict. These issues are one focus of the present work.

Another focus is the matter of control over formation of RuHCl vs RuCl$_2$ products. The conversion of RuCl$_3$·*n*H$_2$O to RuHCl(CO)L$_m$ by tertiary phosphine (L) at reflux in alcoholic solvent rests on a number of critical factors.[5] L must be very bulky if $m = 2$ is to be achieved: the synthesis of *unsaturated*, highly reactive, square-pyramidal RuHCl(CO)L$_2$. A *mono*carbonyl product demands a highly limited source of CO ligand (to avoid formation of saturated RuHCl(CO)$_2$L$_2$), and a primary alcohol furnishes this by C−C bond cleavage (eq 1).

Scheme 1



$$RCH_2OH \rightarrow RH + CO + 2\text{“H”} \qquad (1)$$

The hydride ligand is furnished concurrently, via the dehydrogenation of the alcoholic C$_\alpha$. The processes in Scheme 1 (a) leave the metal oxidation state unchanged and (b) produce equimolar HCl. Point a shows that beginning with commercially available RuCl$_3$·nH$_2$O, that is Ru(III), demands a reducing agent to arrive at Ru(II). This may well be tertiary phosphine (eq 2),

$$R_3P + 2MCl_3 \rightarrow R_3PCl_2 + 2MCl_2 \qquad (2)$$

but the P^V−Cl bonds will be readily hydrolyzed (RuCl$_3$·*n*H$_2$O) to liberate still more HCl, enhancing point b above. In conclusion, the synthesis requires Brønsted base to scavenge liberated HCl. If base is not furnished, eq 3 can cause loss of hydride ligand (as H$_2$) to give a final hydride-free, halide product.

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10.1021/ic000500t CCC: $20.00
Published on Web 11/07/2001

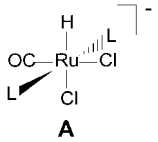
$$M-H + HCl \rightarrow MCl + H_2 \quad (3)$$

A typical example of this is the recent synthesis[6] of $RuCl_2(CO)(P^iPr_2Me)_2$ from $RuCl_3 \cdot nH_2O + 3P^iPr_2Me$ after refluxing for 24 h in $MeOC_2H_4OH$. The beneficial influence of Brønsted base is shown in the recent report[7] that $RuCl_3 \cdot nH_2O + 2.5P^iPr_2Ph$ refluxed for 70 h in MeOH gives $RuCl_2(CO)(P^iPr_2Ph)_2(MeOH)$. In contrast, heating $RuCl_3 \cdot nH_2O + 6P^iPr_2Ph + 2NEt_3$ in MeOH for 5 h gave $RuHCl(CO)(P^iPr_2Ph)_2$. Thus, excess basic phosphine (e.g., $P(alkyl)_3$) and added amine gives a hydride, but the absence of Brønsted bases leads to secondary conversion of hydride to chloride ligand. This conversion was shown independently (eq 4).

$$RuHCl(CO)(P^iPr_2Ph)_2 + HCl \xrightarrow{MeOH} RuCl_2(CO)(MeOH)(P^iPr_2Ph)_2 + H_2 \quad (4)$$

This conversion also shows that the smaller (than P^iPr_3) phosphine permits binding of a sixth ligand like MeOH.

An equally important aspect of success in this synthesis of unsaturated molecules is the need to avoid any nucleophile that might bind to and saturate it. The Lewis acidity of $RuHCl(CO)(P^iPr_2Ph)_2$ (and also the steric accessibility) toward hard nucleophiles is shown by its reaction with $(Ph_3PNPPh_3)Cl$ in benzene to give an anionic adduct, $[PPN][RuHCl_2(CO)(P^iPr_2Ph)_2]$, A. This behavior illustrates another potential pitfall of



A

the synthesis of unsaturated d^6 square-pyramidal species: the formation of a six-coordinate species by coordination of liberated chloride. For comparison, consider[8] the numerous instances where an attempt to use RLi to convert Cp_2MCl to unsaturated Cp_2MR instead produces $Cp_2MRClLi$: chloride is a nucleophile, not a "leaving group".

Small variations in phosphine substituent [note that P^tBu_2Me and P^iPr_3 are isomeric and that P^iPr_3 and PCy_3 (Cy = cyclohexyl) both have secondary alkyl substituents] and small variation in reaction conditions thus can have a large consequence on the resulting products from $RuCl_3 \cdot 3H_2O$ + phosphine. Because various phosphines have been shown to have a large and unpredictable influence on the reactivity of their metal complexes,[9,10] we undertook some comparative experiments on varying phosphine substituent in the hope of deriving some generally useful principles. These are described below, and they reveal that

(1) Na_2CO_3 is superior to NEt_3 for scavenging liberated HCl *and* rendering Cl^- a less-potent ligand for more Lewis acidic Ru;

(2) P^iPr_2Me (cf. P^iPr_3) is small enough to permit dimerization of $RuCl_2(CO)L_2$, and thus *reduced* Lewis acidity;

(3) even the presence of the strong trans effect ligand hydride does not prevent binding of *three* P^iPr_2Me, forming a six-coordinate $RuHCl(CO)(P^iPr_2Me)_3$;

(4) when this $RuHCl(CO)(P^iPr_2Me)_3$ adds Ru−H across the triple bond of $Me_3SiC{\equiv}CH$, the mechanism involves preequilibrium phosphine loss, and the resulting σ-vinyl ligand prevents binding of three P^iPr_2Me in the product; and

(5) comparison of $P^iPr_2(3,5\text{-}(CF_3)_2C_6H_3)$ to P^iPr_3 shows $RuHCl(CO)L_2$ to be more Lewis acidic for the former toward Cl^-.

Taken together, these results show both the importance of coordination number 5 for high reactivity of Ru(II) and the extreme demands on phosphine size which are required to make unsaturated $RuHCl(CO)L_2$ synthetically accessible.

Results

Synthesis with $P^iPr_2[3,5\text{-}(CF_3)_2C_6H_3]$. This phosphine has been chosen to be a weaker donor than $P(alkyl)_3$ and thus perhaps confer greater Lewis acidity on the metal. $P^iPr_2[3,5\text{-}(CF_3)_2C_6H_3]$ was synthesized by reacting P^iPr_2Cl with previously prepared $3,5\text{-}(CF_3)_2C_6H_3MgBr$ (see hazard note in the Experimental Section) with subsequent quenching with aqueous NH_4Cl solution. This previously unknown phosphine was isolated as a liquid and characterized by ^1H, ^{31}P, and ^{19}F NMR. ^1H NMR shows two distinct doublets of doublets for the isopropyl methyls, which is consistent with the absence of a symmetry plane relating the two methyls within a given isopropyl group in the phosphine molecule. Upon exposure to oxygen, this phosphine oxidizes, leading to the formation of the phosphine oxide $O{=}P^iPr_2[3,5\text{-}(CF_3)_2C_6H_3]$ (crystalline solid), which was also characterized by ^1H, ^{31}P, and ^{19}F NMR.

$RuHCl(CO)(P^iPr_2[3,5\text{-}(CF_3)_2C_6H_3])_2$. (a) Attempted Use of the Traditional Synthetic Method. Preparation of $RuHCl(CO)(P^iPr_2[3,5\text{-}(CF_3)_2C_6H_3])_2$ was attempted using the method for the synthesis of $MHCl(CO)L_2$ (L = P^iPr_3, P^tBu_2Me, P^iPr_2Ph; M = Ru, Os): refluxing $RuCl_3 \cdot 3H_2O$ with the phosphine (1:3 mole ratio) in MeOH or $MeOCH_2CH_2OH$ in the presence of NEt_3. However, unlike in the previously reported cases,[7,11] no precipitation of $MHCl(CO)L_2$ was observed upon cooling the reaction solution. ^{31}P NMR analysis of the colorless solid resulting from vacuum removal of solvent revealed the presence of two products with δ (^{31}P) of 50.6 ppm (major) and 44.8 ppm [minor, apparently $RuCl_2(CO)L_2$, based on the similarity of its ^{31}P chemical shift to that of $RuCl_2(CO)(P^iPr_2Ph)_2$, a known byproduct in $RuHCl(CO)(P^iPr_2Ph)_2$ synthesis]. Recrystallization from toluene−pentane mixture allowed the isolation of the δ 50.6 ppm product, which was identified as $[NEt_3H][RuHCl_2(CO)L_2]$. This is formed by addition of $[NEt_3H]Cl$ to $RuHCl(CO)(P^iPr_2[3,5\text{-}(CF_3)_2C_6H_3])_2$ due to its Lewis acidity caused by the presence of strongly electron-withdrawing CF_3 substituents on the phosphine ligands. The unexpectedly good solubility of this ammonium "ruthenate" salt in arene solvents (considering that $[Et_3NH]Cl$ has a very poor solubility in these) can be explained by ion-pairing in solution via hydrogen-bonding between the N−H proton and chlorides on the ruthenium anion. A time evolution study during the synthetic reaction by ^{31}P NMR revealed that the optimal reaction time for the complete conversion to this product, and minimization of the formation of byproducts, is 3 h. This ammonium salt shows a hydride signal at −15.63 ppm (triplet due to coupling to two phosphorus), which is significantly downfield from the ∼ −25 ppm chemical shift for five-coordinate $RuHCl(CO)L_2$ (where there

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is no ligand trans to the hydride) and similar to the previously reported[7] analogous salts [PPN][$RuHCl_2(CO)L_2$] and [MeP^iPr_2Ph][$RuHCl_2(CO)L_2$] (L = P^iPr_2Ph). The presence of NEt_3H^+ in the complex is supported by the observation of a low-field broad signal for the proton on the nitrogen at 10.47 ppm, as well as characteristic peaks for the ethyls. Each of the four diastereotopic methyls of the ^{i}Pr groups shows a doublet of virtual triplets. The IR spectrum in Nujol shows ν(CO) at 1911 cm^{-1}.

(b) Use of Na_2CO_3 as HCl Scavenger. In an attempt to synthesize $RuHCl(CO)L_2$ and avoid the formation of the ammonium ruthenate salt, Na_2CO_3 was used as an HCl scavenger in place of NEt_3. This led to successful synthesis of $RuHCl(CO)(P^iPr_2[3,5\text{-}(CF_3)_2C_6H_3])_2$, isolated as a yellow solid and identified by ^{1}H, ^{31}P, and ^{19}F NMR and IR after 3 h of refluxing in MeOH; a ^{31}P NMR time evolution study showed this to be the optimal reaction time. The hydride chemical shift of this new complex appears at −24.86 ppm, indicative of the hydride being trans to the empty site and very close (within 0.5 ppm) to typical values for known $RuHCl(CO)L_2$ examples. There are also two multiplets, corresponding to two diastereotopic sets of PCH protons of the isopropyl substituents at 2.88 and 2.30 ppm; the methyl region of the ^{1}H NMR spectrum shows the presence of four diastereotopic CH_3 substituents. The IR spectrum in Nujol shows ν(CO) at 1926 cm^{-1}, which is significantly higher than that for the complexes with L = P^iPr_3[11] and P^tBu_2Me[12] and indicative of the weaker donor ability of $P^iPr_2[3,5\text{-}(CF_3)_2C_6H_3]$. This ν(CO) is also higher than for [NEt_3H][$RuHCl_2(CO)L_2$], where Cl^- lowers ν(CO).

Na_2CO_3 is thus seen to be a more effective base than NEt_3 in this synthesis. This must relate to the lower solubility of NaCl than [Et_3NH]Cl and especially to rendering the liberated proton less acidic (by attachment to O^{2-} in the carbonate-derived products $H_2O + CO_2$) than it is in Et_3NH^+. The ammonium cation may retain considerable reactivity of the type shown in eq 3 since it can hydrogen bond to $RuHCl(CO)L_2$ or $RuHCl_2(CO)L_2^-$, thus increasing its potential to liberate H_2.

(c) Lewis Acidity of $RuHCl(CO)(P^iPr_2[3,5\text{-}(CF_3)_2C_6H_3])_2$. The ability of $RuHCl(CO)(P^iPr_2[3,5\text{-}(CF_3)_2C_6H_3])_2$ to add chloride from its ammonium salts, thus supporting the assignment of [NEt_3H][$RuHCl_2(CO)L_2$] as the product of the synthesis in the presence of NEt_3, was studied by reacting this five-coordinate complex with [Bu_4N]Cl. When a benzene-d_6 solution of these two reagents in 1:1 ratio was stirred at 20 °C for 10 min, poorly soluble [Bu_4N]Cl dissolved by reacting, the color changed to nearly colorless, and no precipitate was seen. ^{1}H and ^{31}P NMR indicated complete conversion to [Bu_4N][$RuHCl_2(CO)L_2$], spectroscopically analogous to [NEt_3H][$RuHCl_2(CO)L_2$]. The solubility of the complex in toluene can be explained by ion-pairing. The hydride chemical shift appears at −14.67 ppm as a triplet, while the ^{31}P{^{1}H} NMR chemical shift is at 50.6 ppm.

To study how size and the absence of electron-withdrawing phosphine substituents affects the addition of ammonium chloride salts to $RuHCl(CO)L_2$, the reaction of $RuHCl(CO)(P^iPr_3)_2$ with [Bu_4N]Cl was studied. Visually, after 10 min and after 1 h, the color of a C_6D_6 solution remained unchanged (yellow) and insoluble colorless solid [Bu_4N]Cl remained. ^{1}H and ^{31}P NMR indicated only weak equilibrium binding of the chloride to the metal with only a very low fraction of [Bu_4N][$RuHCl_2(CO)(P^iPr_3)_2$] in the solution; the hydride chemical shift appears at −24.01 ppm as a very broad signal [i.e., only 0.35 ppm downfield from $RuHCl(CO)(P^iPr_3)_2$], and a broad ^{31}P{^{1}H} NMR signal is seen at 57.0 ppm (vs 57.8 ppm for the five-coordinate starting material). This indicates only minor conversion to an adduct and rapid exchange between $RuHCl(CO)(P^iPr_3)_2$ and a trace of its chloride adduct. Evidently, the bulkier and more electron-rich P^iPr_3 ligands decrease the ability of the unsaturated metal complex to add nucleophiles such as chloride. On the basis of these spectral observations, the relative ability of $RuHCl(CO)(P^iPr_2[3,5\text{-}(CF_3)_2C_6H_3])_2$ and $RuHCl(CO)(P^iPr_3)_2$ to add [Bu_4N]Cl was also investigated by internal competition, i.e., mixing these reagents in a 1:1:1 ratio in benzene. ^{1}H and ^{31}P NMR comparison with the spectral data described above showed that [Bu_4N]Cl adds exclusively to $RuHCl(CO)(P^iPr_2[3,5\text{-}(CF_3)_2C_6H_3])_2$ while $RuHCl(CO)(P^iPr_3)_2$ remains intact and shows no sign of any chloride coordination under these conditions, thus indicating significantly higher Lewis acidity of the complex with less electron-rich, smaller phosphine ligands.

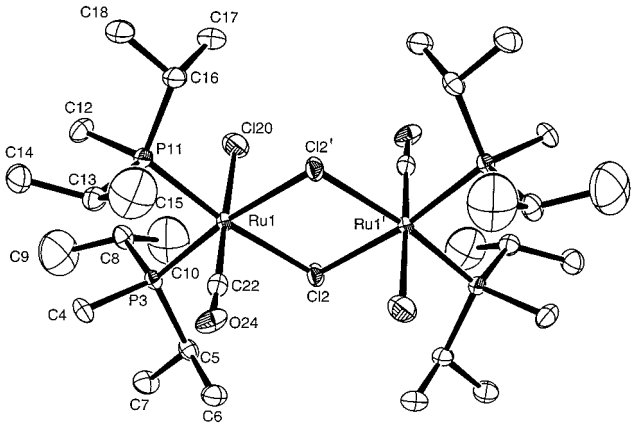

Figure 1. ORTEP view of the nonhydrogen atoms of $[RuCl_2(CO)(P^iPr_2Me)_2]_2$. Primed and unlabeled atoms are related to those indicated by a crystallographic center of symmetry.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[RuCl_2((CO)(P^iPr_2Me)_2]_2$

Ru(1)−Cl(2)	2.4874(9)	Ru(1)−P(11)	2.3203(10)
Ru(1)−Cl(2)′	2.4943(9)	Ru(1)−C(19)	1.773(9)
Ru(1)−Cl(20)	2.436(3)	Ru(1)−C(22)	1.898(10)
Ru(1)−Cl(23)	2.4377(24)	O(21)−C(19)	1.251(9)
Ru(1)−P(3)	2.3182(9)	O(24)−C(22)	1.044(11)
Cl(2)′∠Ru(1)−Cl(2)′	81.63(3)	Cl(2)−Ru(1)−C(22)	88.1(3)
Cl(2)−Ru(1)−Cl(20)	90.63(7)	Cl(2)′∠Ru(1)−C(22)	92.6(3)
Cl(2)′∠Ru(1)−Cl(20)	86.34(7)	Cl(20)−Ru(1)−P(3)	93.53(7)
Cl(2)−Ru(1)−Cl(23)	85.65(9)	Cl(20)−Ru(1)−P(11)	90.12(7)
Cl(2)′∠Ru(1)−Cl(23)	89.58(9)	Cl(20)−Ru(1)−C(22)	178.5(3)
Cl(2)−Ru(1)−P(3)	91.80(3)	Cl(23)−Ru(1)−P(3)	89.74(8)
Cl(2)′∠Ru(1)−P(3)	171.99(3)	Cl(23)−Ru(1)−P(11)	93.57(9)
Cl(2)−Ru(1)−P(11)	172.59(3)	Cl(23)−Ru(1)−C(19)	177.6(3)
Cl(2)′∠Ru(1)−P(11)	91.91(3)	P(3)−Ru(1)−P(11)	94.92(3)
Cl(2)−Ru(1)−C(19)	88.1(3)	Ru(1)−Cl(2)−Ru(1)	98.37(3)
Cl(2)′∠Ru(1)−C(19)	94.5(3)	Ru(1)−C(19)−O(21)	177.2(9)
		Ru(1)−C(22)−O(24)	176.9(11)

A Still Smaller Phosphine: P^iPr_2Me. (a) X-ray Structure and Spectroscopic Characterization of $RuCl_2(CO)(P^iPr_2Me)_2$. Because of the pale yellow color[6] of previously reported $RuCl_2(CO)(P^iPr_2Me)_2$, which suggests the large HOMO/LUMO gap of a saturated complex, we evaluated the hypothesis that the molecule is in fact a dimer. An X-ray structure determination of crystals grown from EtOH/petroleum ether over a period of 10 days showed definitively (Figure 1 and Tables 1 and 2) that the molecule is a dimer, and thus, P^iPr_2Me is small enough that, in the absence of a strong trans effect hydride ligand, dimerization occurs. The dimer has an equilateral $Ru(\mu\text{-}Cl)_2Ru$ core (i.e., edge-shared bioctahedron) with the mutually cis phosphines each trans to the bridging chloride. Each Ru has one terminal Cl and one terminal CO, mutually trans; because these dimers

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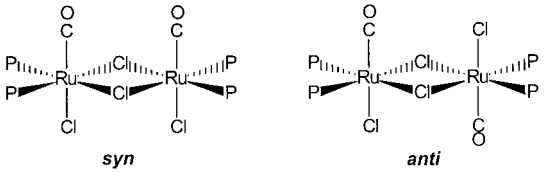
Table 2. Crystallographic Data for $[RuCl_2((CO)(P^iPr_2Me)_2]_2$

formula	$C_{30}H_{68}Cl_4O_2P_4Ru_2$	formula weight	928.71
color	yellow	space group	*C*2/*c*
a, Å	21.773(1)	*T*, °C	100
b, Å	16.215(1)	λ, D	0.710 69
c, Å	12.545(1)	ρ_{calcd}, g/cm^3	1.500
β, Å	111.76(0)	μ(Mo Kα), cm^{-1}	11.75
V, Å^3	4113.33	R	0.0444
Z	4	R_w	0.0424

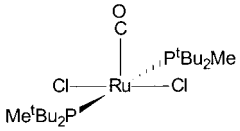
$R = \sum||F_o| - |F_c||/\sum|F_o|$ $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

are located around a crystallographic center of symmetry, these Cl and CO are mutually 50/50 disordered, and thus, syn and anti isomers cannot be distinguished by the X-ray data.



The compact nature of P^iPr_2Me is evident from the ∠P−Ru−P in the dimer: an unexceptional 94.92(3)°. This contrasts to P^iPr_3, which are most often mutually trans. In TpRu-$(H_2O)(P^iPr_2Me)_2^+$, the P−Ru−P angle is 98.54(10)°.[13]

A useful structural comparison compound is monomeric $RuCl_2(CO)(P^tBu_2Me)_2$,[2] **B**. In this compound, the Ru−Cl



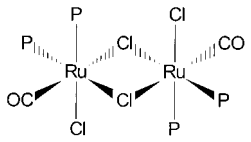
B

distances [2.358(2) and 2.382(3) Å] are shorter than any in $[RuCl_2(CO)(P^iPr_2Me)_2]_2$, due to the trans influence of the carbonyl in the dimer. In the monomer, the Ru−P distances [2.402(3) and 2.406(3) Å] are longer, due to the weaker trans ligands (i.e., μ-Cl) in the dimer.

Since this dimer structure has equivalent phosphines, it cannot be the initial product isolated,[6] which had an AX $^{31}P\{^1H\}$ NMR pattern. We first acted to ascertain the spectroscopic signatures of the crystals employed in the X-ray study. When a crystalline sample of $[RuCl_2(CO)(P^iPr_2Me)_2]_2$ employed in the X-ray study is mixed with CD_2Cl_2 at −70 °C, a partial dissolution of the solid with the formation of a colorless solution is observed. At this temperature, $^{31}P\{^1H\}$ NMR shows only one signal (singlet) at 45.2 ppm, corresponding to the syn or the anti isomer described above, in which all phosphine ligands are equivalent. The ^1H NMR spectrum contains two broad methine multiplets at 2.20 and 2.61 ppm, as well as broad multiplets, corresponding to methyls of phosphine ligands. No significant spectral changes are seen upon gradual warming of this solution to 0 °C. However, upon warming to 20 °C, in addition to the previously present singlet, $^{31}P\{^1H\}$ NMR shows the growth of an AB-pattern at 46.2 and 47.5 ppm (J_{AB} = 26.0 Hz). The presence of a new species is also confirmed by the appearance of an additional methine signal of P^iPr_2Me ligands at 2.40 ppm in ^1H NMR. The singlet and the AB-dimers are present in the mixture in 2:1 molar ratio. Heating of the mixture at 35 °C for 30 min leads to the formation of a homogeneous yellow solution, and this ratio changes to 3:13.

When the crystalline sample is dissolved in CD_3OD at 25 °C, the same two isomers of the Ru dimer are observed. In addition, a $^{31}P\{^1H\}$ NMR singlet is seen at 65.5 ppm; this we attribute to the product of halide bridge splitting by solvent: $RuCl_2(CO)(methanol)(P^iPr_2Me)_2$. We can be certain that this signal is not that of monomeric *trans*-$RuCl_2(CO)(P^iPr_2Me)_2$ because the ^{i}Pr methyl proton resonances, best resolved at 20 °C, show no virtual triplet character diagnostic of mutually trans phosphorus nuclei. This signal is broader than those of the dimer, consistent with dynamic line broadening due to the partial equilibrium MeOH dissociation. The fact that only dimers are seen in CD_2Cl_2 (i.e., 43−47 ppm ^{31}P NMR peaks) indicates that the 65.5 ppm species is not 5-coordinate $RuCl_2(CO)(P^iPr_2Me)_2$ and shows that the dimer is distinctly more stable than any monomer in CD_2Cl_2.

The similarity of all three ^{31}P NMR chemical shifts of the two dimers shows that the local environment, $RuCl_3(CO)P_2$, is the main determinant of the chemical shift. The modest ^{31}P NMR chemical shift differences within the AB dimer suggest that each P is trans to chloride. The same logic suggests that the AB dimer has structure **C**, where each P is trans to Cl (not



C

CO). Structure **C**, a centrosymmetric structure, is preferred on the basis of avoiding steric congestion between syn-oriented axial P^iPr_2Me ligands on two different Ru centers.

Additional evidence for the isomerization of the syn dimer to **C** is provided by IR spectroscopy. The IR spectrum of the original sample used in the X-ray study shows ν(CO) at 1948 cm^{-1} in Nujol. However, in the IR spectrum taken after the variable-temperature NMR study (including 30 min at 35 °C), a new major ν(CO) is observed at 1967 cm^{-1} in CD_2Cl_2. This increase in frequency is indicative of a decrease in the donor power of the ligand (Cl) trans to the carbonyl and is adequately explained by the difference in the structure of the syn dimer vs **C**: while the syn dimer contains CO trans to terminal Cl, in **C** carbonyl is trans to bridging chloride, which decreases the push−pull interaction between Cl and CO ligands, thereby increasing ν(CO).

In summary, $RuCl_2(CO)(P^iPr_2Me)_2$ in noncoordinating solvents appears to exist exclusively, at NMR detection levels, as dimers, but dimers of several stereochemistries, each of which has cis phosphines. The rate of equilibration among the isomeric dimers, as observed in CD_2Cl_2, is no faster than a time scale of minutes at 0−25 °C, but this rate is certainly adequate to account for a low-solution-population isomer to be exclusively the crystalline product.

(b) A Hydrido-Chloride Incorporating P^iPr_2Me. To eliminate the loss of a hydride ligand to HCl [i.e., seeking $RuHCl(CO)(P^iPr_2Me)_2$, which could be a monomer], we conducted the conventional synthetic reaction in methanol with Ru:L ratio = 1:3.5 in the presence of NEt_3. This led to the isolation of a colorless solid that was identified as the 18-electron tris-phosphine complex **D**, $RuHCl(CO)(P^iPr_2Me)_3$, by ^1H and ^{31}P NMR. $^{31}P\{^1H\}$

NMR at 20 °C shows two broad signals at 34.2 ($\Delta\nu_{1/2}$ = 34.7 Hz) and 11.6 ($\Delta\nu_{1/2}$ = 45 Hz) in a 2:1 ratio corresponding to two mutually trans phosphines and the phosphine trans to the hydride, respectively. Lack of observable coupling between phosphorus indicates an equilibrium involving dissociation of

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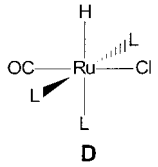


D

the unique phosphine due to the strong trans-influence exerted by the hydride. The hydride signal appears as a broad doublet at −8.38 ppm with J_{HP}(trans) = 108 Hz, which is a typical trans J_{PH} magnitude for phosphine adducts.[14] Cooling to 0 °C slows the exchange: the hydride peak resolves into a doublet of triplets [J_{HP}(cis) = 27 Hz]. The $^{31}P\{^1H\}$ NMR peaks at this temperature transform into a doublet and a triplet, respectively, with $J_{PP'}$ = 17 Hz. The consequence of the presence of three phosphines in the coordination sphere of RuHCl(CO)(P^iPr_2Me)$_3$ is seen in the IR spectrum: ν(CO) is observed at 1898 cm^{-1}, which is lower than for RuHCl(CO)(P^iPr_3)$_2$ (1910 cm^{-1})[11] and RuHCl(CO)(P^tBu_2Me)$_2$ (1904 cm^{-1})[12] and indicative of the presence of a donor ligand trans to the hyride. The presence of three such phosphines in RuHCl(CO)(P^iPr_2Me)$_3$ provides sufficient donation so that ν(CO) for this complex is lower than for any known RuHCl(CO)L$_2$.

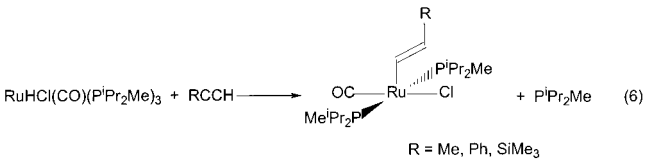
(c) Attempts toward RuHCl(CO)(P^iPr_2Me)$_2$. In an attempt to prevent the formation of this tris phosphine adduct, the Ru:L ratio in the synthesis was changed to 1:2. However, instead of the expected RuHCl(CO)L$_2$, formation of four major hydride-containing products was observed, including RuHCl(CO)L$_3$. All of them had hydride chemical shifts in the −8 to 16 ppm range and thus none of them could be RuHCl(CO)L$_2$; they are perhaps Ru$_2$ species. The third phosphine in RuHCl(CO)(P^iPr_2Me)$_3$ could not be removed by heating the solid compound under vacuum at 80 °C after 24 h or by azeotropic distillation with toluene. In conclusion, P^iPr_2Me is clearly a phosphine small enough to destroy unsaturation by binding *three* phosphines per Ru.

In a "chemical abstraction" attempt to remove the phosphine ligand trans to the hydride, RuHCl(CO)(P^iPr_2Me)$_3$ was reacted with CuBr, a known phosphine-scavenging reagent[15] [i.e., potentially forming CuBr(PR$_3$)$_n$].[16] After 1 h of stirring at 20 °C, the initially colorless solution becomes yellow-orange and ^1H and ^{31}P NMR indicates complete conversion to a different complex, with a broad hydride peak at −15.61 ppm and broad $^{31}P\{^1H\}$ NMR signals at 35.9, 33.4, and 1.6 ppm. The latter chemical shift is indicative of phosphine coordination to copper. Upon cooling to −40 °C, the hydride chemical shift resolves into four unequally intense triplets (J_{PH}) at −15.22, −15.38, −16.00, and −16.16 ppm, and the $^{31}P\{^1H\}$ NMR at this temperature shows four sharp peaks at 37.0, 35.9, 34.5, and 33.4 ppm, in addition to the unchanged high-field signal for phosphine on copper. These spectral data imply that, although the phosphine is "extracted" from ruthenium by copper, the resulting Cu(P^iPr_2Me)Br coordinates to the five-coordinate RuHCl(CO)(P^iPr_2Me)$_2$ with the formation of a halide-bridged complex. This is followed by a halide exchange resulting in four observed hydride complexes of general formula (Me^iPr_2P)-CuRuHX$_2$(CO)(P^iPr_2Me)$_2$, where X = Cl, Br. Reaction of RuHCl(CO)(P^iPr_2Me)$_3$ with CuCl gives the spectral simplification expected for elimination of mixed-halide analogues. In conclusion, phosphine "abstraction" from RuHCl(CO)(P^iPr_2Me)$_3$ is unsuccessful.

(d) Reactivity of RuHCl(CO)(P^iPr_2Me)$_3$: Does the Sixth Ligand Poison Reactivity? To understand the effect of the presence of the third phosphine ligand trans to the hydride, we studied the reactivity of saturated RuHCl(CO)(P^iPr_2Me)$_3$ toward a variety of small molecules. Addition of two equiv. of H_2, C_2H_4, or Me_3SiH to a solution of RuHCl(CO)(P^iPr_2Me)$_3$, followed by mixing for 30 min at room temperature does not lead to any ^1H or ^{31}P NMR spectral change, which is indicative of the absence of any reactions with these gaseous reagents. These results are consistent with an analogous behavior of RuHCl(CO)L$_2$ (L = P^tBu_2Me,[17] P^iPr_3[11] which are also completely unreactive toward these molecules under similar conditions. This lack of reactivity shows that, although the unsaturated five-coordinate complex RuHCl(CO)(P^iPr_2Me)$_2$ is present in solution due to equilibrium 5, binding of σ-donating but bulkier P^iPr_2Me is preferred over H_2, C_2H_4 and Me_3SiH, despite the steric hindrance created by the two phosphine ligands in this complex.

$$\mathrm{RuHCl(CO)(P^iPr_2Me)_3} \rightleftharpoons \mathrm{RuHCl(CO)(P^iPr_2Me)_2} + \mathrm{P^iPr_2Me} \quad (5)$$

In contrast, reaction of RuHCl(CO)(P^iPr_2Me)$_3$ with propyne is complete in 30 min at +20 °C and leads to the formation (eq 6) of red five-coordinate vinyl complex Ru(*E*-CH═CHCH$_3$)(CO)(Cl)(P^iPr_2Me)$_2$,which was characterized by ^1H and ^{31}P NMR. ^1H NMR shows a doublet at 7.06 ppm ($J_{HH(trans)}$ = 12.0 Hz) and a multiplet at 5.02 ppm, corresponding to the protons on the C$_\alpha$ and C$_\beta$ atoms of the vinyl fragment. In addition to the signal of the vinyl complex at 28.6 ppm, $^{31}P\{^1H\}$ NMR also displays a peak at −10.0 ppm, characteristic of free P^iPr_2Me. This result indicates that the absence of a free coordination site in RuHCl(CO)(P^iPr_2Me)$_3$ does not prevent the insertion of the alkyne into the Ru−H bond and that the methylvinyl ligand has a sufficiently stronger trans effect than hydride, to give an unsaturated five-coordinate species instead of a six-coordinate trisphosphine vinyl complex.



Reaction of RuHCl(CO)(P^iPr_2Me)$_3$ with phenylacetylene also occurs very fast, resulting within 10 min at room temperature in complete transformation to Ru(*E*-CH═CHPh)(CO)(Cl)-(P^iPr_2Me)$_2$. The protons on C$_\alpha$ and C$_\beta$ atoms of the vinyl fragment in this case appear as doublets ($J_{HH(trans)}$ = 13.7 Hz) at a significantly lower field (8.95 and 6.52 ppm) than the propenyl analogue due to the electron-withdrawing effect of the phenyl substituent. The implied Lewis acidity is also evident in the $^{31}P\{^1H\}$ NMR spectrum: unlike in the case of the methylvinyl complex described above, signals for both the vinyl complex at 28.2 ppm and the free P^iPr_2Me are broadened. This is explained by an equilibrium process involving coordination and dissociation of the phosphine to the metal center trans to the more electron-withdrawing phenylvinyl ligand.

Influence of the steric bulk of the substituent on the alkyne is clearly seen in reaction of RuHCl(CO)(P^iPr_2Me)$_3$ with trimethylsilylacetylene. Insertion of acetylene into the Ru−H bond here occurs at a significantly lower rate: after 1 h at room temperature, only 20% conversion of the starting material to Ru(*E*-CH═CHSiMe$_3$)(CO)(Cl)(P^iPr_2Me)$_2$ is found by ^1H and ^{31}P NMR. Even after 120 h at room temperature, only 68%

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conversion to the vinyl complex is observed. Unlike in the case of more Lewis acidic Ru(*E*-CH=CHPh)(CO)(Cl)(P^{i}Pr$_2$Me)$_2$, no ^{31}P NMR line broadening due to the coordination of the third phosphine is seen in the evolving reaction mixture.

The observed order of rates for the alkynes containing electronically and sterically different substituents with six-coordinate RuHCl(CO)(P^{i}Pr$_2$Me)$_3$ (Ph> Me>SiMe$_3$) is similar to that found in reactions of five-coordinate MHCl(CO)L$_2$ (M = Os, Ru; L = P^{t}Bu$_2$Me, P^{i}Pr$_3$).[18] The addition of excess free P^{i}Pr$_2$Me strongly suppresses the rate of the reaction of RuHCl(CO)(P^{i}Pr$_2$Me)$_3$ with Me$_3$SiCCH. When these two reagents are reacted in a 1:1 ratio with no added phosphine, 36% conversion (based on ^{31}P NMR integration) to Ru(CH=CHSiMe$_3$)(CO)(P^{i}Pr$_2$Me)$_2$ is observed after 18 h at 20 °C. If this reaction is conducted in the presence of a 4-fold excess of free P^{i}Pr$_2$Me, only 5% conversion to the same product is observed after this time period. This is consistent with eq 5 being crucial to the alkyne insertion in the Ru−H bond. Apparently it is the more flexible structure of the square-pyramidal intermediate RuHCl(CO)(P^{i}Pr$_2$Me)$_2$ (in comparison to octahedral RuHCl(CO)(P^{i}Pr$_2$Me)$_3$) that allows a direct alkyne attack on the Ru−H fragment.

Conclusions

One conclusion from this work is that, even when L′ = Cl$^-$, P^{i}Pr$_2$Me, or MeOH binds to a RuHCl(CO)L$_2$ species, the binding is weak. That is, although the equilibrium position lies to the left in eq 6,

$$\mathrm{RuHCl(CO)L_2L'} \overset{k_1}{\rightleftharpoons} \mathrm{RuHCl(CO)L_2} + \mathrm{L'} \qquad (6)$$

k_1 is large enough at 20 °C to let the equilibrium system react rapidly with substrates (L″) and to show dynamic NMR phenomena in the absence of L″. On the other hand, and highly dependent on the properties of L, eq 6 can lead to isolation of six-coordinate products from the traditional synthesis originally devised for the bulky phosphines PCy$_3$, P^{i}Pr$_3$, and P^{t}Bu$_2$Me. The weakness of binding L′ is due to the open coordination site trans to the (reactive) hydride ligand, but the generally stronger binding to MHCl(CO)L$_2$ for M = Os (vs Ru) makes loss of unsaturation (i.e., the binding of L′) more likely for osmium.

The structural study of the RuCl$_2$(CO)(P^{i}Pr$_2$Me)$_2$ species shows that this phosphine is small enough to permit dimerization, with concomitant *cis*-phosphine stereochemistry. This emphasizes the narrow range of phosphine steric bulk that permits isolation of unsaturated RuXCl(CO)L$_2$ species (X = H or Cl) using traditional synthetic methods: it is only phosphine steric bulk that can overcome the Lewis acidity of 16-electron Ru(II).

The use of a fluorinated aryl group in P^{i}Pr$_2$R enables the synthesis of unsaturated RuHCl(CO)L$_2$ reagents, whose Lewis acidity shows the transmission of electronic effects from the 3,5-(CF$_3$)$_2$C$_6$H$_3$ group R.

Experimental Section

General Considerations. All reactions and manipulations were conducted using standard Schlenk and glovebox techniques under prepurified argon. Solvents were dried and distilled under argon and stored in airtight solvent bulbs with Teflon closures. All NMR solvents were dried, vacuum-transferred, and stored in a glovebox. ^{1}H, ^{31}P, and ^{19}F spectra were recorded on a Varian Gemini 300 and on a Varian Inova 400 instruments. Chemical shifts are referenced to residual solvent (^{1}H), external H$_3$PO$_4$ (^{31}P), or external CF$_3$CO$_2$H (^{19}F). RuHCl(CO)(P^{i}Pr$_3$)$_2$ was prepared according to a published procedure.[10]

P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$]. A dark-brown solution of the Grignard reagent 3,5-(CF$_3$)$_2$C$_6$H$_3$MgBr in 200 mL of Et$_2$O was prepared using 25 g (0.085 mol) of 3,5-(CF$_3$)$_2$C$_6$H$_3$Br and 2.6 g (0.11 mol) of Mg according to a published procedure.[19] Explosions involving solid (CF$_3$)$_2$C$_6$H$_3$MgBr have been reported, so the Et$_2$O solution employed here must not be taken to dryness. A solution of 13 g (0.085 mol) of P^{i}Pr$_2$Cl in 100 mL of Et$_2$O was slowly added dropwise while the flask was cooled with cold water. The reaction mixture was then gently refluxed for 20 h. After cooling, the reaction was quenched by addition of a degassed, saturated NH$_4$Cl solution (30 g in 110 mL H$_2$O) with ice bath cooling. The Et$_2$O layer was decanted off, and the aqueous layer was washed with Et$_2$O (2 × 50 mL). The wash was added to the original Et$_2$O layer and the solution was concentrated at 5 °C. After concentrating the solution to ∼100 mL, it was dried by stirring with Na$_2$SO$_4$. After decanting the solution off Na$_2$SO$_4$, Et$_2$O was removed in vacuo at 5 °C. This resulted in the formation of spectroscopically pure P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$] as a viscous liquid (14 g, 50%). ^{1}H NMR (C$_6$D$_6$, 20 °C), ppm: 0.59, 0.77 (both dd, J_{HP} = 11.7 Hz, J_{HH} = 6.9 Hz, PCHC*H*$_3$), 1.62 (m, PC*H*), 7.68 (s, *p*-hydrogen of 3,5-(CF$_3$)$_2$C$_6$*H*$_3$), 7.82 (d, J_{HP} = 4.8 Hz, *o*-hydrogens of 3,5-(CF$_3$)$_2$C$_6$H$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C): 12.3 (s). ^{19}F{^{1}H} (C$_6$D$_6$, 20 °C): −64.8 (s).

A solution of P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$] in C$_6$D$_6$ exposed to air slowly (∼7 d) oxidizes with the formation of phosphine oxide O=P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$] (observed by NMR). ^{1}H NMR (C$_6$D$_6$, 20 °C), ppm: 0.63, 0.66 (both dd, J_{HP} = 15.3 Hz, J_{HH} = 6.9 Hz, PCC*H*$_3$), 1.69 (m, PC*H*), 7.88 (d, J_{HP} = 4.5 Hz, *p*-3,5-(CF$_3$)$_2$C$_2$H$_2$*H*), 8.18 (d, J_{HP} = 8.9 Hz, *o*-3,5-(CF$_3$)$_2$C$_6$*H*$_2$H). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C), ppm: 48.5. ^{19}F-{^{1}H} NMR (C$_6$D$_6$, 20 °C), ppm: −64.6.

[NEt$_3$H][RuHCl$_2$(CO)(P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$])$_2$]. RuCl$_3$·3H$_2$O (1.7 g; 6.4 mmol) was mixed with triethylamine (3.4 g; 15 mmol) and P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$] (6.5 g; 20 mmol), and 2-methoxyethanol (60 mL) was added via cannula. The resulting solution was heated at 120 °C for 21 h. Volatiles were removed in vacuo, and the residue was dissolved in a minimum amount of hot toluene. Pentane was added to the solution, and cooling to −40 °C afforded a colorless precipitate, which was filtered and washed with 10 mL of pentane. Yield: 3.8 g (61%). ^{1}H NMR (C$_6$D$_6$, 20 °C), ppm: −15.63 (t, J_{HP} = 23.1 Hz, Ru*H*), 0.67 (t, J_{HH} = 6.0 Hz, [N(CH$_2$C*H*$_3$)$_3$H]), 0.99, 1.11, 1.32, 1.51 (all dvt, J_{HH} = 7.5 Hz, N = 7.8 Hz, PCHC*H*$_3$), 2.11 (br, m, N(C*H*$_2$CH$_3$)$_3$H]), 2.55, 3.34 (both m, PC*H*), 7.81, 9.15 (both s, −3,5-(CF$_3$)$_2$C$_6$*H*$_3$), 10.47 (br, [Et$_3$N*H*]). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C): 50.6 (82%, RuHCl$_2$(CO)(P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$])$_2^-$); 44.8 (18%, RuCl$_2$(CO)(P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$])]$_2$). ^{19}F{^{1}H} NMR (C$_6$D$_6$, 20 °C): −64.3. IR (Nujol): ν(CO) = 1911 cm^{-1}.

RuHCl(CO)(P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$])$_2$. RuCl$_3$·3H$_2$O (0.5 g; 1.9 mmol) was mixed with P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$] (2.1 g; 6 mmol) and Na$_2$CO$_3$ (0.2 g; 2 mmol), and methanol (25 mL) was added via cannula. The resulting solution was refluxed at 70 °C for 8 h. Volatiles were removed in vacuo, and the resulting solid was dissolved in benzene and filtered via glass wool. Benzene then was removed in vacuo and the residue was washed with pentane (2 × 5 mL). This resulted in yellow-orange solid product. Yield: 1.02 g (65%). ^{1}H NMR (C$_6$D$_6$, 20 °C), ppm: −24.86 (t, J_{HP} = 18.8 Hz, Ru*H*), 0.66, 0.88, 1.03 (double intensity), (all m, PCHC*H*$_3$), 2.30, 2.88 (both m, PC*H*), 7.71, 8.22 (double intensity) (both s, 3,5-(CF$_3$)$_2$C$_6$*H*$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C): 60.5. ^{19}F{^{1}H} NMR (C$_6$D$_6$, 20 °C): −63.6. IR (Nujol): ν(CO) = 1926 cm^{-1}.

[Bu$_4$N][RuHCl$_2$(CO)(P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$])$_2$]. RuHCl(CO)(P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$])$_2$ (15 mg; 0.018 mmol) was added to 5 mg (0.018 mmol) of [Bu$_4$N]Cl and dissolved in 0.5 mL of benzene-d_6 in an NMR tube. After mixing for 10 min at 20 °C, the reaction mixture became homogeneous and the color of the solution changed from yellow-orange to nearly colorless. ^{1}H NMR (C$_6$D$_6$, 20 °C), ppm: −14.67 (t, J_{HP} = 22.5 Hz, Ru*H*), 0.90 (t, J_{HH} = 6.6 Hz, [N(CH$_2$CH$_2$CH$_2$C*H*$_3$)$_4$]), 1.11, 1.23, 1.35, 1.51 (all m, PCHC*H*$_3$, [N(CH$_2$C*H*$_2$C*H*$_2$CH$_3$)$_4$]), 2.63, 3.28 (m, PC*H*), 3.11 (t, J_{HH} = 7.5 Hz), [N(C*H*$_2$CH$_2$CH$_2$CH$_3$)$_4$]), 7.86, 9.34 (double intensity) (both s, 3,5-(CF$_3$)$_2$C$_6$*H*$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C): 50.6. ^{19}F{^{1}H} NMR (C$_6$D$_6$, 20 °C): −62.4.

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Reaction of [Bu$_4$N]Cl with RuHCl(CO)(P^{i}Pr$_3$)$_2$. RuHCl(CO)(P^{i}Pr$_3$)$_2$ (15 mg; 0.031 mmol) was added to 8.6 mg (0.031 mmol) of [Bu$_4$N]Cl and dissolved in 0.5 mL of benzene-d_6 in an NMR tube. After mixing for 10 min or 1 h at 20 °C, the color remains yellow-orange and the reaction mixture is still heterogeneous due to undissolved [Bu$_4$N]Cl. NMR indicates the presence of only a very low fraction of [Bu$_4$N][RuHCl$_2$(CO)(P^{i}Pr$_3$)$_2$]. ^{1}H NMR (C$_6$D$_6$, 20 °C), ppm: −24.01 (br, $\Delta\nu_{1/2}$ = 188 Hz, RuH), 0.99 (t, J_{HH} = 6.6 Hz, [N(CH$_2$CH$_2$-CH$_2$C*H*$_3$)$_4$]), 1.22−1.33 (m, PCHC*H*$_3$, [N(CH$_2$C*H*$_2$C*H*$_2$C*H*$_3$)$_4$]), 2.57 (br, PC*H*), 3.19 (br, m, [N(CH$_2$CH$_2$C*H*$_2$CH$_3$)$_4$]). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C): 57.0 (br, $\Delta\nu_{1/2}$ = 116 Hz).

Competition Reaction of RuHCl(CO)(P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$])$_2$ and RuHCl(CO)(P^{i}Pr$_3$)$_2$ with [Bu$_4$N]Cl. RuHCl(CO)(P^{i}Pr$_3$)$_2$ (10.8 mg; 0.022 mmol) was mixed with 18 mg (0.022 mmol) of RuHCl(CO)-(P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$])$_2$ and with 6 mg (0.022 mmol) of [Bu$_4$N]Cl in 0.5 mL of benzene-d_6 in an NMR tube. The reaction mixture becomes heterogeneous (yellow-orange) after mixing for 15 min at 20 °C, and ^{1}H and ^{31}P{^{1}H} NMR indicate the presence of [Bu$_4$N][RuHCl$_2$(CO)-(P^{i}Pr$_2$[3,5-(CF$_3$)$_2$C$_6$H$_3$])$_2$] and unreacted RuHCl(CO)(P^{i}Pr$_3$)$_2$.

Variable-Temperature NMR Study of [RuCl$_2$(CO)(P^{i}Pr$_2$Me)$_2$]$_2$. To an NMR tube, cooled to −196 °C and containing 15 mg (0.016 mmol) of crystalline [RuCl$_2$(CO)(P^{i}Pr$_2$Me)$_2$]$_2$, was vacuum-transferred 0.5 mL of CD$_2$Cl$_2$. The sample was thawed briefly and then shaken several times to allow for mixing and inserted into a precooled NMR probe. The solution at −70 °C was colorless and most of the complex did not dissolve. ^{1}H NMR (CD$_2$Cl$_2$, −70 °C), ppm: 1.20, (br m, PC*H*$_3$, PCHC*H*$_3$), 2.20, 2.61 (both br m, PC*H*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −70 °C): 45.2 (s). No significant spectral changes were observed in the −70 to 0 °C temperature range. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C), ppm: 1.19−1.47 (overlapping m, PC*H*$_3$, PCHC*H*$_3$), 2.25, 2.40, 2.62 (all m, PC*H*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 70 °C) (121.4 Hz): 44.8 (s, 66%), 46.2, 47.5 (AB pattern, J_{AB} = 26.0 Hz, 34%). After heating for 30 min at 35 °C, the molar ratio of the singlet and the AB dimers in the mixture is 3:13. The solution at this temperature is homogeneous and yellow.

RuHCl(CO)(P^{i}Pr$_2$Me)$_3$. RuCl$_3$·3H$_2$O (1.0 g; 3.8 mmol) was mixed with triethylamine (1.1 g; 10.5 mmol) and P^{i}Pr$_2$Me (1.8 g; 13.6 mmol), and methanol (30 mL) was added via cannula. The resulting solution was heated at 65 °C for 8 h. Volatiles were removed in vacuo, and the resulting residue was dissolved in toluene and filtered via a frit. After toluene was removed by heating at 55 °C for 5 h under vacuum, the solid was washed with 10 mL of pentane, yielding a mostly colorless residue. Yield: 1.3 g (62%). ^{1}H NMR (C$_6$D$_6$, 20 °C), ppm: −8.38 (br d, $\Delta\nu_{1/2}$ = 191 Hz, $J_{HP(trans)}$ = 108 Hz, Ru*H*), 1.10−1.34, (overlapping m, PC*H*$_3$, PCHC*H*$_3$), 2.02, 2.21, 2.36 (all m, PC*H*). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C): 11.6 (br, $\Delta\nu_{1/2}$ = 45 Hz, RuP^{i}Pr$_2$Me trans to the hydride), 34.2 (br, $\Delta\nu_{1/2}$ = 35 Hz, Ru(P^{i}Pr$_2$Me)$_2$ cis to the hydride). ^{1}H NMR (CD$_2$Cl$_2$, 0 °C), ppm: −8.35 (dt, $J_{HP(trans)}$ = 108 Hz, $J_{HP(cis)}$ = 27.0 Hz, Ru*H*), 1.15−1.36 (overlapping m, PC*H*$_3$, PCHC*H*$_3$), 2.10, 2.25, 2.30 (all m, PC*H*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 0 °C): 11.6 (t, J_{PP} = 17 Hz, RuP^{i}Pr$_2$Me trans to the hydride), 34.1 (d, J_{PP} = 17 Hz, Ru(P^{i}Pr$_2$-Me)$_2$ cis to the hydride).

Reaction of RuHCl(CO)(P^{i}Pr$_2$Me)$_3$ and CuBr. RuHCl(CO)(P^{i}Pr$_2$-Me)$_3$ (15 mg; 0.027 mmol) was added to 10 mg (0.069 mmol) of CuBr in 0.5 mL of toluene-d_6 in an NMR tube. The color of the reaction mixture changed from colorless to orange after mixing for 1 h at 20 °C. ^{1}H NMR (C$_7$D$_8$, −40 °C), ppm: −16.16, −15.99, −15.38, −15.22 (all t, J_{HP} = 19.8 Hz, RuH), 0.61−1.73 (overlapping m, PC*H*$_3$, PCHC*H*$_3$), 2.41 (br, PC*H*). ^{31}P{^{1}H} NMR (C$_7$D$_8$, −40 °C): 1.7 (br, $\Delta\nu_{1/2}$ = 134 Hz, CuP^{i}Pr$_2$Me), 33.4, 34.5, 35.9, 37.0 (all s, Ru(P^{i}Pr$_2$-Me)$_2$).

X-ray Diffraction Structure Determination of [RuCl$_2$(CO)-(P^{i}Pr$_2$Me)$_2$]$_2$.[1] Single crystals of the dimeric compound suitable for X-ray structure analysis were obtained directly from the mother liquor, by concentration of the 2-methoxyethanol solution, diluting with EtOH, and layering with petroleum ether. Slow diffusion over a period of ca. 10 days at room temperature afforded single crystals of the dimeric compound (20% yield). The sample consisted of yellow transparent crystals of varying sizes growing in clumps. One of the larger crystals was selected, and a well-formed fragment cleaved from a section that appeared to be flawless. The sample was then affixed to the glass fiber on a goniometer head and transferred to the goniostat, where it was cooled to −158 °C for characterization and data collection (Table 2). A set of frames from three orthogonal sections of reciprocal space was used to determine that the crystal possessed monoclinic symmetry with systematic absences corresponding to either space group *C*2/*c* or its noncentrosymmetric equivalent, *Cc*. Subsequent solution and refinement confirmed the centrosymmetric choice, *C*2/*c*. The data were collected using a Bruker-AXS SMART6000 CCD area detector system. A complete hemisphere of data was collected using 0.3° ω scans. Data were reduced using the Bruker-AXS SAINT series of programs. The structure was solved using direct methods (SHELXTL) and Fourier techniques. There was a disorder involving the terminal chlorine atom and carbonyl group that was easily modeled. Although hydrogen atoms were readily located in a difference synthesis, several did not converge properly. In the final cycles of refinement, all hydrogen atoms were allowed to vary isotropically except for those associated with C(9), C(10), and C(15). Hydrogen atoms associated with these three carbons were placed in fixed, idealized positions. A final difference Fourier was featureless, the largest peak being 0.55 e/Å^3.

Reactions of RuHCl(CO)(P^{i}Pr$_2$Me)$_3$ with H$_2$, C$_2$H$_4$, and SiMe$_3$H. RuHCl(CO)(P^{i}Pr$_2$Me)$_3$ (15 mg; 0.027 mmol) was dissolved in 0.5 mL of benzene-d_6 in three NMR tubes. The solutions were freeze−pump−thaw degassed and H$_2$, C$_2$H$_4$, or SiMe$_3$H was condensed in the tubes using a vacuum line (gas:Ru molar ratio = 2:1). After 30 min of mixing at 20 °C, ^{1}H and ^{31}P NMR showed only the presence of starting materials in all three cases.

Reaction of RuHCl(CO)(P^{i}Pr$_2$Me)$_3$ with Propyne. RuHCl(CO)-(P^{i}Pr$_2$Me)$_3$ (15 mg; 0.027 mmol) was dissolved in 0.5 mL of benzene-d_6 in an NMR tube. The solution was freeze−pump−thaw degassed and propyne was condensed in the tube using a vacuum line (MeC≡CH:Ru molar ratio = 2:1). The color of the reaction mixture changed from colorless to red after mixing for 30 min at 20 °C, and the formation of Ru(*E*-CH=CHCH$_3$)(CO)(Cl)(P^{i}Pr$_2$Me)$_2$ was observed by NMR. ^{1}H NMR (C$_6$D$_6$, 20 °C), ppm: 1.03−1.39 (m, PCHC*H*$_3$, PC*H*$_3$), 1.84 (d, J_{HH} = 6.0 Hz, Ru−CH=CHC*H*$_3$), 2.73 (m, PC*H*), 5.02 (m, Ru−CH=C*H*−), 7.06 (d, J_{HH} = 12.0 Hz, Ru−C*H*=). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C), ppm: 28.6 (s, Ru(*E*-CH=CHCH$_3$)(CO)(Cl)(P^{i}Pr$_2$Me)$_2$), −10.0 (s, free P^{i}Pr$_2$Me).

Reaction of RuHCl(CO)(P^{i}Pr$_2$Me)$_3$ with Phenylacetylene. RuHCl-(CO)(P^{i}Pr$_2$Me)$_3$ (15 mg; 0.027 mmol) was added to 2.6 μL (0.027 mmol) of PhC≡CH in 0.5 mL of benzene-d_6 in an NMR tube. The color of reaction mixture changed from colorless to red after mixing for 10 min at 20 °C and the formation of Ru(*E*-CH=CHPh)(CO)(Cl)-(P^{i}Pr$_2$Me)$_2$ was observed by NMR. ^{1}H NMR (C$_6$D$_6$, 20 °C), ppm: 1.10−1.31 (m, PC*H*$_3$, PCHC*H*$_3$), 2.14, 2.84 (each m, PC*H*), 6.52 (d, J_{HH} = 13.6 Hz, Ru−CH=C*H*−), 7.08−7.59 (m, Ru−CH=CH*Ph*), 8.95 (d, J_{HH} = 13.6 Hz, Ru−C*H*=). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C), ppm: 28.2 (br, Ru(*E*-CH=CHPh)(CO)(Cl)(P^{i}Pr$_2$Me)$_2$), −10.0 (br, free P^{i}Pr$_2$-Me).

Reaction of RuHCl(CO)(P^{i}Pr$_2$Me)$_3$ with Trimethylsilylacetylene. RuHCl(CO)(P^{i}Pr$_2$Me)$_3$ (15 mg; 0.027 mmol) was added to 3.8 μL (0.027 mmol) of Me$_3$SiC≡CH in 0.5 mL of benzene-d_6 in an NMR tube. No visual changes were observed immediately upon mixing. After mixing for 1 h at 20 °C, 20% conversion to Ru(*E*-CH=CHSiMe$_3$)-(CO)(Cl)(P^{i}Pr$_2$Me)$_2$ was observed by NMR. ^{1}H NMR (C$_6$D$_6$, 20 °C), ppm: 0.11 (−SiMe$_3$), 0.97−1.35 (m, PC*H*$_3$, PCHC*H*$_3$), 2.38, 2.84 (each m, PC*H*), 5.60 (d, J_{HH} = 13.2 Hz, Ru−CH=C*H*−), 8.59 (d, J_{HH} = 13.2 Hz, Ru−C*H*=). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C), ppm: 29.2 (s, Ru-(*E*-CH=CHSiMe$_3$)(CO)(Cl)(P^{i}Pr$_2$Me)$_2$), −10.2 (s, free P^{i}Pr$_2$Me). After 120 h at 20 °C, ^{31}P{^{1}H} NMR shows 68% conversion to Ru(*E*-CH=CHSiMe$_3$)(CO)(Cl)(P^{i}Pr$_2$Me)$_2$.

Acknowledgment. This work was supported by the U.S. Department of Energy.

Supporting Information Available: Crystallographic data for [RuCl$_2$(CO)(P^{i}Pr$_2$Me)$_2$]$_2$ in CIF format.This material is available free of charge via the Internet at http://pubs.acs.org.

IC000500T