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Agostic Bonding in Pincer Complexes of Ruthenium

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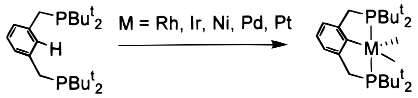
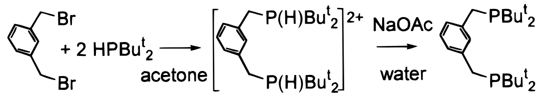
High-yield preparations have been developed for 16-e square-pyramidal complexes of ruthenium(II) RuCl(CO)[2,6-$(CH_2PBu^t{}_2)_2C_6H_3$] (**1**), RuHCl[1,3-$(CH_2PBu^t{}_2)_2C_6H_4$] (**2**), and RuHI[1,3-$(CH_2PBu^t{}_2)_2C_6H_4$] (**3**). NMR and X-ray studies have revealed strong η^2 CH bonding in the Ru[1,3-$(CH_2PBu^t{}_2)_2C_6H_4$] fragment of **2** and **3**. These complexes show stretched agostic C−H bonds, elongated ipso-C−Ru distances, reduced $^1J_{CH}$ couplings, and large IPR shifts in ^{1}H NMR. A consistent picture has emerged of a stronger agostic bonding and greater C−H bond activation in the η^2 C−H trans to chloride in **2**. This finding is attributed to stronger π-donor properties of chloride compared to iodide and increased back-donation into the antibonding orbital of the η^2 C−H. Analysis of the X-ray and NMR T_1 data has also indicated the presence of an attractive interaction, *dihydrogen* bonding, between the agostic C−H hydrogen and neighboring hydride in **2** and **3**.

1. Introduction

Bulky diphosphines 1,3-$(CH_2PR_2)_2C_6H_4$ (R = Bu^t, Cy, Pr^i) are now increasingly used in coordination chemistry with late transition metals.[1−3] The best studied in the series is 1,3-$(CH_2PBu^t{}_2)_2C_6H_4$ (D^{t}BPX, di-*tert*-butylphosphinoxylene), synthesized by Moulton and Shaw in 1976.[1a] D^{t}BPX typically undergoes metalation and coordinates in a tridentate PCP-fashion to give 16-e "pincer" complexes, e.g., MX(PCP) (M = Ni, Pd, Pt; X = H, halide) and MHCl(PCP) (M = Rh, Ir; PCP = [2,6-$(CH_2PBu^t{}_2)_2C_6H_3]^-$).[1a] Recent research with pincer complexes has been focused on the subject of C−E bond activation (E = H, C, O).[3e,4] The iridium dihydrides IrH_2(PCP) (R = Pr^i, Bu^t) have attracted much attention as active catalysts for homogeneous dehydrogenation of hydrocarbons.[4c,d,i]



Scheme 1



While group 9 and 10 metal compounds with bulky PCP ligands have been studied extensively, reactions of these ligands with group 8 metals remain virtually unexplored.[3d] In this paper, we report an improved preparation of 1,3-$(CH_2PBu^t{}_2)_2C_6H_4$ and describe first ruthenium complexes with this diphosphine: RuCl(CO)(PCP) (**1**) and RuHX[1,3-$(CH_2PBu^t{}_2)C_6H_4$] (X = Cl (**2**), I (**3**)). Of the new compounds, complex **1** is formed by the cyclometalated PCP = [2,6-$(CH_2PBu^t{}_2)_2C_6H_3]^-$, while **2** and **3** contain an elongated η^2 agostic C−H bond of the coordinated D^{t}BPX ligand.

2. Results

2.1. Preparation of 1,3-$(CH_2PBu^t{}_2)_2C_6H_4$. The original synthesis of D^{t}BPX was accomplished by the quaternization of di-*tert*-butylphosphine with α,α′-dibromo-*m*-xylene and subsequent deprotonation of the diphosphonium salt with sodium acetate, according to Scheme 1.[1a] This approach involves the isolation of [1,3-$(CH_2P(H)Bu^t{}_2)_2C_6H_4]Br_2$, and the product needs to be extracted from the aqueous reaction mixture and purified by Kugelrohr distillation to obtain crystalline D^{t}BPX.

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[†] Wilfrid Laurier University

[‡] Institute of Organoelement Compounds (crystal structure analyses of **2** and **3**).

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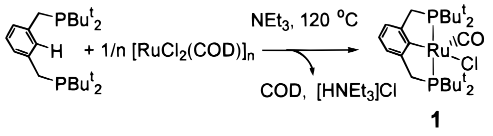
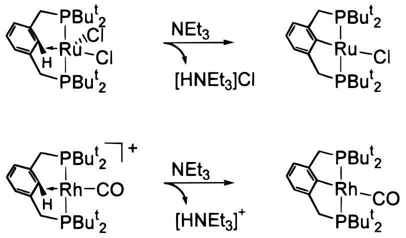
Scheme 2



Scheme 3

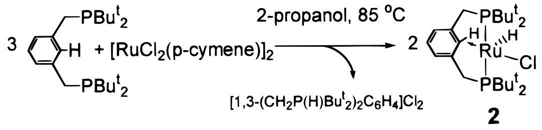


In our modified procedure, the quaternization is carried out in methanol. The intermediate salt is deprotonated by triethylamine in situ; D^{t}BPX precipitates and is isolated by filtration. Di-*tert*-butylphosphine can be obtained by the treatment of ClPBu$^t_2$ with $LiAlH_4$ in ether[5] or without solvent (see Experimental Part).

2.2. Reactions of D^{t}BPX with $RuCl_3{\cdot}3H_2O$, [RuCl$_2$(COD)]$_n$, and [RuCl$_2$(*p*-cymene)]$_2$. Several known pincer complexes of ruthenium have been derived from 1,3-(CH_2PPh_2)$_2C_6H_4$ and $RuCl_2(PPh_3)_3$ via RuCl(PPh$_3$)[2,6-(CH_2PPh_2)$_2C_6H_3$].[6] To prepare new molecules containing two P atoms per metal, we investigated reactions of the bulkier 1,3-($CH_2P^tBu_2$)$_2C_6H_4$ with convenient starting materials containing no phosphine: $RuCl_3{\cdot}3H_2O$, [RuCl$_2$(COD)]$_n$, and [RuCl$_2$(*p*-cymene)]$_2$. In the initial experiments, when a solution of $RuCl_3{\cdot}3H_2O$ in ethanol was heated with D^{t}BPX, only a black insoluble material precipitated. This reaction, however, afforded the brown *cis*-RuCl(CO)(PCP) (**1**) in 68% yield in the presence of triethylamine. Complex **1** was obtained in a better yield (84%) from [RuCl$_2$(COD)]$_n$ and an equivalent amount of NEt_3 in isoamyl alcohol at 120 °C (Scheme 2). Complex **1** is an air-stable solid and is slightly air-sensitive in solution.

The role of triethylamine in the above reactions of $RuCl_3{\cdot}3H_2O$ and [RuCl$_2$(COD)]$_n$ deserves a comment. We know that 2-methylpyridine promoted cyclometalation when $RhCl_3{\cdot}nH_2O$ was treated with 1,5-bis(di-*tert*-butylphosphino)pentane.[7] Rapid ArCH$_2$−H bond activation of 1,3,5-(CH_3)$_3$-2,6-($CH_2PPr^i_2$)$_2C_6H$ was observed with $RuCl_2(PPh_3)_2$ in the presence of ^{t}BuONa.[3d] Mechanistically, elimination of hydrogen chloride in these reactions can explain the need for a sacrificial base. Thus, formation of **1** from [RuCl$_2$(COD)]$_n$ and D^{t}BPX likely proceeds by COD displacement via RuCl$_2$(D^{t}BPX), which can be deprotonated by NEt_3 to give another intermediate, [RuCl(PCP)] (Scheme 3). There is an analogy here with the behavior of [Rh(CO)(D^{t}BPX)]$^+$ that affords Rh(CO)(PCP) when treated with triethylamine.[1d] The η^2 C−H fragment can be sufficiently acidic to be deprotonated by a nitrogen base.

Scheme 4



The 14-e RuCl(PCP) can further react with a primary alcohol to abstract CO. If the decarbonylation is unlikely, as from secondary alcohols, only dehydrogenation of the solvent might be expected.[8] This was indeed observed upon heating D^{t}BPX and [RuCl$_2$(*p*-cymene)]$_2$ in 2-propanol under nitrogen. The ruthenium product RuHCl[1,3-($CH_2PBu^t_2$)$_2C_6H_4$] (**2**) was isolated as a brown crystalline solid (Scheme 4). This preparation afforded **2** in a better yield when carried out under hydrogen. Complex **2** can be obtained from [RuCl$_2$(COD)]$_n$, but this reaction is very slow.

The chloride **2** is converted into the corresponding iodide RuHI[1,3-$CH_2PBu^t_2$)$_2C_6H_4$] (**3**) in methyl iodide. Both **2** and **3** are air-sensitive solids that turn black in 1 and 20 min, respectively, the iodide being appreciably more stable toward oxidation.

Compounds **1**, **2**, and **3** were characterized by elemental analysis, NMR techniques, and X-ray crystallography. The molecular structures are shown in Figure 1, and selected bond distances and angles are listed in Table 1.

3. Discussion

3.1. Crystal Structures of Complexes 1−3. The square-pyramidal structure of RuCl(CO)[2,6-($CH_2PBu^t_2$)$_2C_6H_3$] shows a well-defined basal plane formed by the chloride, two phosphorus, and carbon atoms of the [2,6-($CH_2PBu^t_2$)$_2C_6H_3$]$^-$ ligand; the carbonyl is in the apical position. Complex **1** can be compared to the related compound RuCl(PPh$_3$)[2,6-(CH_2PPh_2)$_2C_6H_3$] (**4**) (Scheme 5).[6] When the identity of the apical ligands in **1** and **4** is disregarded, the two molecules appear isostructural. The ruthenium−ipso-carbon bond lengths are the same (2.076(4) in **1** vs 2.070(4) Å in **4**).[6d] This single C−Ru bond lies essentially in the aromatic plane of the [2,6-($CH_2PBu^t_2$)$_2C_6H_3$]$^-$ ligand.

Related square-pyramidal compounds with monodentate phosphines RuCl(*p*-tolyl)(CO)(PPh$_3$)$_2$,[9a] RuCl(*o*-tolyl)(CO)(PPh$_3$)$_2$,[9a] and RuCl(Ph)(CO)(PMeBu$^t_2$)$_2$[9b] have a different ligand disposition with the chloride trans to CO (e.g., OC−Ru−Cl 167.1° in RuCl(Ph)(CO)(PMeBu$^t_2$)$_2$). We note that the empty coordination site trans to CO in **1** is shielded by two bulky Bu^t groups (Figure 1) and is probably disfavored for steric reasons. Although there must be some repulsion between the Bu^t groups and CO as well, the carbonyl is less likely to reorient trans to the ipso-carbon because of the strong trans influence of these ligands.

Figure 1 shows that the heavy atoms P(1), P(2), and Cl(1) occupy almost identical positions around ruthe-

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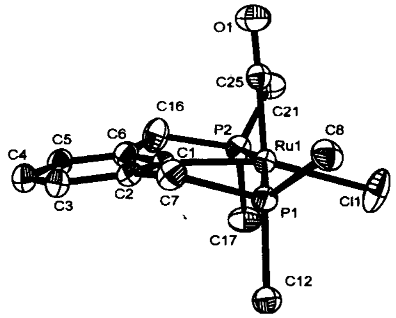
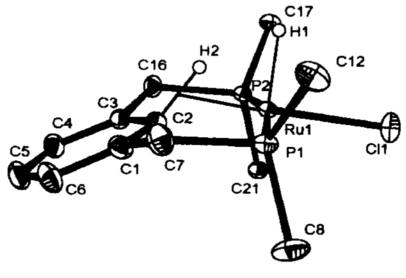
Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 1−3

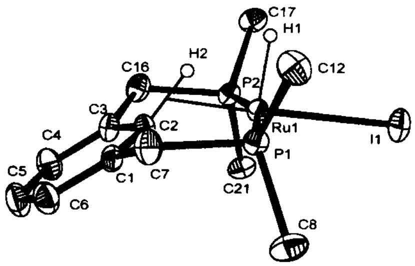
complex **1**		complex **2**		complex **3**	
Ru(1)−C(1)	2.076(4)	Ru(1)−C(2)	2.115(3)	Ru(1)−C(2)	2.135(4)
Ru(1)−C(25)	1.757(5)	Ru(1)−H(1)	1.52(4)	Ru(1)−H(1)	1.42(4)
Ru(1)−Cl(1)	2.420(1)	Ru(1)−Cl(1)	2.388(1)	Ru(1)−I(1)	2.713(1)
Ru(1)−P(1)	2.383(1)	Ru(1)−P(1)	2.345(1)	Ru(1)−P(1)	2.369(1)
Ru(1)−P(2)	2.370(1)	Ru(1)−P(2)	2.339(1)	Ru(1)−P(2)	2.351(1)
C(25)−O(1)	1.183(6)	C(2)−H(2)	1.31(5)	C(2)−H(2)	1.32(4)
		Ru(1)−H(2)	1.53(5)	Ru(1)−H(2)	1.53(4)
C(1)−Ru(1)−C(25)	85.0(2)	C(2)−Ru(1)−H(1)	103(2)	C(2)−Ru(1)−H(1)	107(2)
C(1)−Ru(1)−Cl(1)	164.34(12)	C(2)−Ru(1)−Cl(1)	165.15(8)	C(2)−Ru(1)−I(1)	165.06(11)
C(1)−Ru(1)−P(1)	85.53(13)	C(2)−Ru(1)−P(1)	82.83(9)	C(2)−Ru(1)−P(1)	82.51(11)
C(1)−Ru(1)−P(2)	83.09(13)	C(2)−Ru(1)−P(2)	82.99(9)	C(2)−Ru(1)−P(2)	82.06(11)
C(25)−Ru(1)−P(1)	95.01(15)	H(1)−Ru(1)−P(1)	94.2(1)	H(1)−Ru(1)−P(1)	97(2)
C(25)−Ru(1)−P(2)	93.7(2)	H(1)−Ru(1)−P(2)	94.2(1)	H(1)−Ru(1)−P(2)	90(2)
C(25)−Ru(1)−Cl(1)	110.6(2)	H(1)−Ru(1)−Cl(1)	92(2)	H(1)−Ru(1)−I(1)	88(2)
P(1)−Ru(1)−P(2)	162.44(4)	P(1)−Ru(1)−P(2)	164.86(3)	P(1)−Ru(1)−P(2)	164.29(4)
Cl(1)−Ru(1)−P(1)	94.74(5)	Cl(1)−Ru(1)−P(1)	96.08(4)	I(1)−Ru(1)−P(1)	97.30(3)
Cl(1)−Ru(1)−P(2)	96.39(5)	Cl(1)−Ru(1)−P(2)	96.26(4)	I(1)−Ru(1)−P(2)	96.84(4)
		H(1)−Ru(1)−H(2)	65(2)	H(1)−Ru(1)−H(2)	69(2)
		C(2)−Ru(1)−H(2)	38(2)	C(2)−Ru(1)−H(2)	38(2)
		Ru(1)−C(2)−H(2)	46(2)	Ru(1)−C(2)−H(2)	45(2)



RuCl(CO)[2,6-($CH_2PBu^t_2$)$_2C_6H_3$] (**1**)



RuHCl[1,3-($CH_2PBu^t_2$)$_2C_6H_4$] (**2**)



RuHI[1,3-($CH_2PBu^t_2$)$_2C_6H_4$] (**3**)

Figure 1. Molecular structure and partial atom labeling scheme for complexes **1**−**3**. Nonmetal hydrogens and methyl groups are omitted for clarity.

nium in **1** and **2**. These complexes however display a major difference that arises as a consequence of the (formal) replacement of CO by H_2. While one of the two hydrogen atoms takes up the apical position, the other establishes a bonding interaction with the C(2) carbon. This η^2 C−H bond is trans to the halide that makes **2** and **3** closely resemble the η^2 H−H complex RuH(H_2)I(PCy_3)$_2$ (**5**) characterized by X-ray (Scheme 6).[10]

Scheme 5

1 **4**

Scheme 6

3 **5**

The η^2 C−H in **3** and η^2 H−H in **5** are significantly elongated: 1.32(5) Å (vs 1.08 Å in C_6H_6) and 1.03(7) Å (vs 0.74 Å in free H_2), respectively.[10] Another common feature of **3** and **5** is the relatively short C−H···H−Ru and H−H···H−Ru distances determined as 1.68(7) Å in **3** and 1.66(6) Å in **5**. The latter is a consequence of weak bonding generally encountered between H and cis-H_2.[10] It appears that the agostic C−H is similarly interacting with the neighboring hydride. This C−H···H−Ru bonding can be envisioned as intermolecular *dihydrogen* bonding[11] and might explain the particular geometry of **2** and **3** where the C−H is directed toward the hydride and not toward the empty coordination site.

The C(2)−H(2) distances in **2** and **3** cannot be reliably compared by X-ray and appear similar: 1.31(5) and 1.32(4) Å. The C(2)−Ru(1) distance is longer in the iodide compound: 2.135(4) (**3**) > 2.115(3) Å (**2**). Further analysis of the Ru[1,3-($CH_2PBu^t_2$)C_6H_4] unit shows that ruthenium is removed from the aromatic plane by 22.2° in **3** and 15.6° in **2**. These observations constitute substantial evidence of a stronger agostic interaction in **2**. We believe that the η^2 C−H is slightly more activated when trans to chloride because of the stronger π-donor ability of this ligand compared to iodide.[12] In part, the

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stronger agostic bonding in **2** can also be attributed to the slightly weaker trans effect of Cl^- vs I^-.

Larger molecular distortions have been observed in the agostic pincer complex $Rh(CO)[1,3\text{-}(CH_2PBu^t_2)_2C_6H_4]^+$ (shown in Scheme 3), where the metal is removed from the aromatic plane by 41°.[1d] This molecule has a long Rh−C distance of 2.273(5) Å and a short C−H bond. Another related pincer complex, $Ru[2,6\text{-}(CH_2PPh_2)_2C_6H_3][1,3\text{-}(CH_2PPh_2)_2C_6H_4]^+$, shows an even longer agostic Ru−C distance of 2.395(4) Å and probably only very weak η^2 C−H bonding that could not be characterized by spectroscopic means.[13]

3.2. Structure of Complexes 1−3 in Solution. Major structural features deduced from the NMR spectra of **1**, **2**, and **3** are in agreement with the X-ray data. These species possess inequivalent Bu^t groups since the P−C−P ligand plane is not a molecular symmetry plane. Complexes **2** and **3** show one triplet resonance in the hydride region, close to −16 ppm. It has the intensity of 2H and belongs to the rapidly exchanging terminal hydride and agostic hydrogen. The hydride-coupled ^{31}P NMR spectra are also observed as triplets, i.e., effectively coupled to two ^1H spins. Neither the hydrides **2** and **3** nor their deuterated isotopomers showed decoalescence at low temperature. Even at −100 °C there was no unusual broadening in the hydride region of the ^1H NMR spectra and decoalescence might be unobservable in solution. This rapid reversible C−H fission followed by H/H scrambling is consistent with the significant elongation of the agostic C−H bond and relatively short C−H···H−Ru contact observed by X-ray. Two related fluxional cyclometalated hydrides, $RhHCl[CH(C_2H_4PBu^t_2)_2]$ and $IrH_2[CH(C_2H_4PBu^t_2)_2]$, show fast C−H/M−H exchange above −30 °C.[7,14]

Definitive evidence for stretched C−H bonds in **2** and **3** in solution was provided by the ^1H-coupled ^{13}C NMR spectra, where triplet resonances of the η^2 C−H showed averaged $J_{CH} = (^1J_{CH} + ^2J_{CH})/2$ couplings of 21 and 24 Hz, respectively. The $^2J_{CH}$ hydride coupling is probably small and might be negative. We have recently observed a $|^2J_{CH}|$ of 5 Hz in $[RuH(C_2Ph)(CO)(PCP)]^-$, where the hydride is cis to the ipso-carbon.[15] Using this value for $^2J_{CH}$, the one-bond C−H coupling $^1J_{CH}$ is estimated as ca. 52 and 58 Hz in **2** and **3**, respectively. The other known agostic pincer complexes $Rh(CO)[1,3\text{-}(CH_2PBu^t_2)_2C_6H_4]^+$ and $IrH_2[CH(C_2H_4PBu^t_2)_2]$ have larger $^1J_{CH}$ couplings of 123 and 104 Hz, respectively, corresponding to short C−H bonds.[1d,14]

Agostic (η^2-CH)M bonding is fundamentally analogous to the binding of dihydrogen, (η^2-H_2)M.[16] Given the observation of the larger $^1J_{CH}$ in the iodide **2**, it is interesting that osmium complexes *trans*-$[OsX(\eta^2\text{-}HD)(NH_3)_4]^+$ and *trans*-$[OsX(\eta^2\text{-}HD)(en)_2]^+$ demonstrate an analogous trend of increasing $^1J_{HD}$ for heavier halides (e.g., 10.2 (Cl), 11.8 (Br), and 12.5 Hz (I) in the former).[12] When these couplings are interpreted in terms of the H−D distances,[17] the smallest $^1J_{HD}$ translates into the most stretched η^2 H−D, trans to Cl. In a qualitative molecular orbital consideration this is explained by enhanced back-bonding from the metal to the σ^*_{HH} orbital caused by efficient π-donation of the chloride.[16]

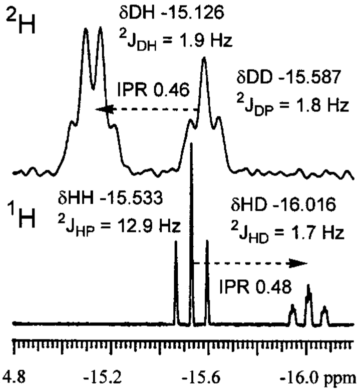

Figure 2. ^1H and ^2H NMR spectra of partially deuterated **2** in dichloromethane.

Additional structural information was sought in the ^1H and ^2H spectra of partially deuterated **2** and **3**. They show well-resolved resonances of the d_0, d_1, and d_2 isotopomers (Figure 2). We note a small H−D coupling in **2**-d_1, in agreement with the assignment of **2** and **3** as agostic rather than dihydrogen complexes. The ^1H T_1(min) times are 72 and 240 ms in **2**-d_0 and **2**-d_1, respectively (at 200 MHz). With these relaxation times, the CH···HRu separation of 1.65 Å can be calculated,[18] similar to the 1.64(6) Å distance between the agostic hydrogen and hydride determined by X-ray.

NMR spectra in Figure 2 show significant shifts of the d_1 isotopomers, known as IPR (isotopic perturbation of resonance). The low-field ^2H shift and the high-field ^1H shift are in agreement with the thermodynamic preference for deuterium to reside on carbon. On lowering the temperature, the observed IPR increased for the chloride **2**: 0.494 (20 °C), 0.527 (5 °C), 0.562 (−10 °C), 0.601 (−25 °C), 0.630 (−40 °C). The iodide **3** demonstrated a similar trend: 0.673 (25 °C), 0.753(5 °C), 0.813 (−10 °C), 0.872 (−25 °C), 0.937 (−40 °C). This is expected in a two-site system, where IPR is a function of temperature: $IPR = 0.5(\delta_{CH} - \delta_{RuH})(K - 1)/(K + 1)$, where $K = \exp(\Delta E/RT)$, $\Delta E = E(RuDX(D^tBPX)) - E(RuHX(D^tBPX\text{-}d))$.[19a]

IPR data have been used for determination of the chemical shifts and ΔE in complexes with agostic methyl groups.[19b] These *three* unknowns can be calculated from the *three* averaged ^1H shifts: $\delta(d_0)$, $\delta(d_1)$, and $\delta(d_2)$. Unfortunately, there are only *two* observables, $\delta(d_0)$ and $\delta(d_1)$, for **2** and **3,** and neither the shifts δ_{CH} and δ_{RuH} nor ΔE could be derived from the IPR data in this work.

Only a semiquantitative analysis of the isotopic shifts can be attempted, based on the observation that the hydride is trans to an empty coordination site in **2** and **3**. This is associated with large negative shifts in square-

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pyramidal geometry; for example, RuHCl(Ph)(PMeBu$^t_2$)$_2$ shows the hydride at −28.6 ppm.[9b] If δ_{RuH} is ca. −28.6 in our system, the chemical shift can be estimated for the agostic hydrogen: δ_{CH} −2.5 in **2** and δ_{CH} −3.4 in **3**, since $\delta_{CH} = 2\delta_{av} - \delta_{RuH}$. The equilibrium constants and ultimately ΔE values can be further derived, and we calculated $\Delta E \approx 44$ cal/mol in **2** and $\Delta E \approx 63$ cal/mol in **3**. The smaller IPR in **2** (e.g., 0.630 vs 0.937 ppm in **3** at −40 °C) appears to be primarily due to stronger agostic bonding to ruthenium and therefore weaker carbon−hydrogen bonding in the η^2 C−H fragment of **2**.

4. Concluding Remarks

Pursuing a program of exploratory synthetic research with pincer complexes of ruthenium, we have developed efficient preparations of new compounds RuCl(CO)[2,6-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_3$] (**1**), RuHCl[1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$] (**2**), and RuHI[1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$] (**3**). Complexes **1**−**3** have been structurally characterized and can be described as square-pyramidal 16-e complexes of Ru(II). Two most interesting molecules of this work are the hydrides **2** and **3**, where one coordination site is occupied by an agostic C−H bond. These unusual new compounds demonstrate a remarkable tendency of ruthenium to retain its stable oxidation state +2 even in a coordinatively unsaturated and sufficiently electron-rich environment.

The properties of the η^2 C−H fragment in **2** and **3** have been thoroughly investigated by X-ray and other spectroscopic techniques (VT NMR, T_1 relaxation, C−H coupling, IPR). A consistent picture has thus emerged of a stronger agostic bonding and greater C−H bond activation in the η^2 C−H trans to chloride in **2**. This finding is attributed to stronger π-donor properties of chloride compared to iodide and, hence, increased back-donation into the antibonding orbital of η^2 C−H.

Experimental Part

General Comments. All room-temperature reactions and NMR sample preparations were done under nitrogen in a glovebox equipped with a vacuum line and a −35 °C refrigerator. When heating was required, the reaction mixtures were prepared in the box, then transferred out, attached to a manifold, and opened under N$_2$ (or H$_2$). The reaction vessels were returned into the box for isolation of the products. All deuterated and regular solvents were rigorously dried then stored and used in the glovebox. NMR measurements were done on a Varian VXR 200 spectrometer. Throughout this paper, the NMR data are reported with the apparent coupling of observed virtual triplets (vt) denoted as ^vJ. Hydrated ruthenium trichloride was purchased from Pressure Chemicals and [RuCl$_2$(*p*-cymene)]$_2$ from Strem, whereas other chemicals were received from Aldrich. The polymeric [RuCl$_2$(COD)]$_n$ was prepared according to a published procedure.[20]

Preparation of HPBu$^t_2$. LiAlH$_4$ (0.8 g, 21.1 mmol) was added in portions to neat ClPBu$^t_2$ (14 g, 77.5 mmol) upon stirring. This mixture was stirred for 25 h. (Note: although this reaction does not appear to be exothermic, cautious addition of LiAlH$_4$ is advisable). The resulting suspension was degassed by three freeze−pump−thaw cycles (0.01 mmHg), and the product was vacuum-transferred into another flask immersed in liquid N$_2$. During the transfer, the reaction flask was kept at room temperature for 30 min and then at 50−60 °C until only a dry residue remained. Yield: 7.8 g (69%). ^{1}H NMR (C$_6$D$_6$): δ 1.14 (d, $^3J_{HP} = 11.8$ Hz, 18H, C*H*$_3$), 3.16 (d, $^1J_{HP} = 210.2$ Hz, 1H, P*H*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 20.0.

Preparation of 1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$. 1,3-Bis(bromethyl)-benzene (7 g, 26.5 mmol) was added to HPBu$^t_2$ (7.76 g, 53.1 mmol). The mixture was diluted with methanol (20 mL) and stirred for 19 h. (In the first 30 min this reaction is exothermic and the solvent may boil for a short time.) To the resulting solution was added NEt$_3$ (5.56 g, 54.9 mmol), and a white solid precipitated when the reaction mixture was stirred with a spatula. It was isolated by filtration, washed with 3 × 10 mL of methanol, and dried under vacuum for 3 h. Yield: 8.4 g (80%). ^{1}H NMR (C$_6$D$_6$): δ 1.07 (d, $^3J_{HP} = 10.5$ Hz, 18H, C*H*$_3$), 2.77 (d, $^2J_{HP} = 2.5$ Hz, 4H, C*H*$_2$), 7.15 (m, 1H, C$_6$*H*$_3$), 7.29 (m, 2H, C$_6$*H*$_3$), 7.61 (s, 1H, C$_6$*H*$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 33.5.

Preparation of RuCl(CO)[2,6-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_3$] (1). *Method 1.* A suspension containing RuCl$_3$·3H$_2$O (1.32 g, 5.05 mmol), 1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$ (2 g, 5.07 mmol), and NEt$_3$ (1.08 g, 10.67 mmol) in ethanol (30 mL) was stirred for 28 h at 80 °C. The solids were filtered off, washed with 3 × 5 mL of ethanol, and dried. The product was purified by filtration of its solution in CH$_2$Cl$_2$, followed by evaporation in vacuo. Yield: 1.78 g (68%). *Method 2.* [RuCl$_2$(COD)]$_n$ (1.10 g, 3.93 mmol [Ru]), 1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$ (1.63 g, 4.13 mmol), and NEt$_3$ (0.4 g, 3.95 mmol) were reacted for 24 h at 120 °C in a mixture of ethanol (3 mL) and isoamyl alcohol (17 mL). The product precipitated when the flask was left overnight at 0 °C. It was isolated by filtration, washed with 4 × 4 mL of methanol, and dried under vacuum for 4 h. Yield: 1.85 g (84%). Anal. Calcd. for C$_{25}$H$_{43}$ClOP$_2$Ru (558.09): C, 53.80; H, 7.77. Found: C, 54.03; H, 7.73. IR (Nujol): ν_{CO} 1909 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 1.10, 1.34 (vt, $^vJ = 6.5$ Hz, 36H, C*H*$_3$), 3.13 (overlapped, 4H, C*H*$_2$), 7.06 (m, 3H, C$_6$*H*$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 69.0. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 29.88, 30.22 (vt, $^vJ = 2.3$ Hz, *C*H$_3$), 35.12 (vt, $^vJ = 10.6$ Hz, *C*H$_2$), 36.88 (vt, $^vJ = 7.5$ Hz, P*C*), 37.24 (vt, $^vJ = 7.0$ Hz, P*C*), 122.83 (vt, $^vJ = 7.6$ Hz, *C*H, Ar), 124.21 (s, *C*H, Ar), 152.37 (vt, $^vJ = 7.0$ Hz, *C*, Ar), 166.62 (t, $^2J_{CP} = 1.6$ Hz, Ru*C*), 209.14 (t, $^2J_{CP} = 12.6$ Hz, *C*O).

Preparation of RuHCl[1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$] (2). A mixture of [RuCl$_2$(*p*-cymene)]$_2$ (1.21 g, 1.98 mmol) and C$_6$H$_4$-1,3-(CH$_2$PBu$^t_2$)$_2$ (2.34 g, 5.93 mmol) in 15 mL of 2-propanol was stirred under hydrogen for 45 h at 85 °C. After cooling, the reaction mixture was left overnight at room temperature. The product precipitated and was isolated by filtration, washed with 3 × 3 mL of methanol, and dried in vacuo for 3 h. Yield: 1.78 g (85%). Anal. Calcd for C$_{24}$H$_{45}$ClP$_2$Ru (532.09): C, 54.18; H, 8.52. Found: C, 54.21; H, 8.48. IR (Nujol): ν_{RuH} 2114 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ −15.53 (t, $^2J_{HP} = 13.0$ Hz, 2H, (η^2-C*H*)-Ru*H*), 1.27, 1.34 (vt, $^vJ = 6.4$ Hz, 36H, C*H*$_3$), 3.06 (m, 4H, C*H*$_2$), 6.93 (m, 1H, *Ar*), 7.07 (m, 2H, *Ar*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 63.7. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 29.60, 30.17 (vt, $^vJ = 2.9$ Hz, *C*H$_3$), 33.61 (vt, $^vJ = 9.4$ Hz, *C*H$_2$), 33.95 (vt, $^vJ = 7.2$ Hz, P*C*), 37.70 (vt, $^vJ = 5.7$ Hz, P*C*), 123.45 (vt, $^vJ = 7.0$ Hz, *C*H, Ar), 124.93 (s, *C*H, Ar), 152.02 (t, $^2J_{CP} = 1.5$ Hz, Ru(*C*H)), 154.99 (vt, $^vJ = 7.4$ Hz, *C*, Ar).

Preparation of RuHI[1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$] (3). The chloride RuHCl[1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$] (0.2 g, 0.38 mmol) was dissolved in 5 mL of CH$_3$I and left at room temperature for 48 h. Then this solution was filtered through Celite, all volatiles were removed in vacuo, and the residue was washed with 3 and 1.5 mL of 2-propanol and dried in vacuo. Yiled: 0.2 g (85%). Anal. Calcd for C$_{24}$H$_{45}$IP$_2$Ru (623.54): C, 46.23; H, 7.27. Found: C, 45.84; H, 7.16. IR (Nujol): ν_{RuH} 2100 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, −30 °C): δ −16.01 (t, $^2J_{HP} = 12.5$ Hz, 2H, (η^2-C*H*)-Ru*H*), 1.24, 1.35 (vt, $^vJ = 6.4$ Hz, 36H, C*H*$_3$), 3.06 (m, 4H, C*H*$_2$), 7.06 (s, 3H, *Ar*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 62.1.

Preparation of Partially Deuterated 2 and 3. These samples were prepared in dichloromethane under deuterium gas in 5-mm NMR tubes. They were degassed by five freeze−pump−thaw cycles prior to measurement.

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Table 2. Crystallographic Data for Complexes 1−3

	1	2	3
formula	$C_{25}H_{43}ClOP_2Ru$	$C_{24}H_{45}ClP_2Ru$	$C_{24}H_{45}IP_2Ru$
fw	558.05	532.06	623.51
cryst syst	orthorombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/n$	$P2_1/n$
a, Å	11.512(2)	7.815(3)	16.017(3)
b, Å	15.847(3)	24.141(9)	10.823(2)
c, Å	29.829(4)	13.992(6)	16.527(3)
α, deg	90	90	90
β, deg	90	94.46(3)	108.74(3)
γ, deg	90	90	90
V, Å^3	5441.8(16)	2632(2)	2713.1(9)
Z	8	4	4
D(calcd), g/cm^3	1.362	1.343	1.526
abs coeff, mm^{-1}	0.806	0.827	1.842
no. of total reflns	4782	6520	5947
no. of unique reflns	3613	6088	5739
R,[a] %	4.64	4.68	3.28
R_w,[a] %	13.03	11.94	8.09

[a] All data collected with Mo Kα radiation ($\lambda = 0.71069$ Å), $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

Crystal Structure Determination. X-ray quality crystals of **1**−**3** were obtained by recrystallization of the complexes from ethanol (**1** and **2**) and $(Et_2OCH_2CH_2)_2O$ (**3**).

Standard geometrical calculations were done using the program PLATON compiled for IBM-PC.[21]

Complex 1. The diffraction experiment was performed on a Siemens SMART System CCD diffractometer at room temperature. The SMART software was used for data collection, and the SAINT program was used for data reduction. An empirical absorption correction was applied, and the structure was solved by direct methods using the SHELXTL suite of programs. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in the ideal positions and refined as riding atoms. Crystal data and details of the data collection are summarized in Table 2.

Complex 2. The diffraction experiment was performed on a Siemens P3/PC diffractometer at 170 K. Accurate unit cell parameters and orientation matrixes were obtained by least-squares refinement of 24 carefully centered reflections in the 25° ≤ 2θ ≤ 29° range. Two standard reflections were monitored every 98 reflections and showed no significant variations. Data were corrected for Lorenz and polarization effects. A carefully chosen small, well-formed, and essentially isometric single-crystal sample as well as the quality of the obtained results and the relatively low values of the absorption coefficient justified no need for absorption correction. The structure was solved by direct methods and from successive difference Fourier map calculations. All hydrogen atoms were located from the difference Fourier synthesis and were refined isotropically. All calculations were carried out on an IBM PC with SHELXTL PLUS 5 programs. Crystal data and details of the X-ray experiment are given in Table 2.

Complex 3. Experimental data were collected on a four-circle automatic diffractometer Enraf-Nonius CAD4 (22 °C, Mo Kα monochromatic radiation, $\theta/2\theta$ scan, $2\theta \leq 54°$). The empirical absorption correction (μ(Mo Kα) = 18.42 cm^{-1}) based on the azimuthal scans of 16 reflections was applied. The structure was solved by direct methods and refined by a full-matrix least-squares analysis using anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms bonded to ruthenium atoms were unambiguously located in the difference Fourier map and were refined using isotropic approximation; all other H atoms were placed in calculated positions and refined in the riding model approximation. All calculations were carried out using the SHELXTL PLUS program package. Important details of the data collection and structure refinement are summarized in Table 2.

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Supporting Information Available: Tables of atomic coordinates, bond lengths, angles, and anisotropic thermal parameters as well as three X-ray crystallographic files for **1**−**3**, in CIF format. This material is available free of charge via Internet at http://pubs.acs.org.

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