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Unsaturated Ru(0) Species with a Constrained Bis-Phosphine Ligand: $[Ru(CO)_2(^tBu_2PCH_2CH_2P^tBu_2)]_2$. Comparison to $[Ru(CO)_2(P^tBu_2Me)_2]$

Torsten Gottschalk-Gaudig,[‡] John C. Huffman,[‡] Hélène Gérard,[†] Odile Eisenstein,[*,†] and Kenneth G. Caulton[*,‡]

Department of Chemistry and Molecular Structure Center, Indiana University,
Bloomington, Indiana 47405-4001, and LSDSMS (UMR 5636), Université de Montpellier 2,
34095 Montpellier Cedex 5, France

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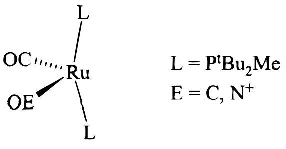
The synthesis of $Ru(C_2H_4)(CO)_2(d^tbpe)$ ($d^tbpe = {}^tBu_2PC_2H_4P^tBu_2$), then green $[Ru(CO)_2(d^tbpe)]_n$ is described. In solution, $n = 1$, while in the solid state, $n = 2$; the dimer has two carbonyl bridges. DFTPW91, MP2, and CCSD(T) calculations show that the potential energy surface for bending one carbonyl out of the $RuP_2C(O)$ plane is essentially flat. $Ru(CO)_2(d^tbpe)$ reacts rapidly in benzene solution to oxidatively add the H−E bond of H_2, HCl, HCCR (R = H, Ph), $[HOEt_2]BF_4$, and $HSiEt_3$. The H−C bond of C_6HF_5 oxidatively adds at 80 °C. CO adds, as does the C=C bond of $H_2C{=}CHX$ (X = H, F, Me). The following do not add: N_2, THF, acetone, H_3COH, and H_2O.

Introduction

We have reported earlier on the synthesis, structure, and reactivity of $Ru(CO)_2(P^tBu_2Me)_2$[1] and its isoelectronic analogue $Ru(CO)(NO)(P^tBu_2Me)_2{}^+$.[2] These are rare examples of unsaturated, zerovalent ruthenium complexes. We have moreover shown that, unlike the typical planar structure of d^8 $M(CO)Cl(PR_3)_2$, M = Rh or Ir, and $M'Cl_2(PR_3)_2$, M′ = Pd or Pt, these zerovalent ruthenium species with two π-acid ligands adopt a structure which resembles a trigonal bipyramid with an empty equatorial site, **I**. While this has the advantage of minimizing the inter-phosphine repulsion, ab initio calculations have shown that the same structure is adopted for L = PH_3; thus, this structure originates from *electronic,* not steric, preferences.



L = P^tBu_2Me
E = C, N^+

I

We explore here the consequences of linking together the two phosphine donors, via the ligand $^tBu_2PCH_2CH_2P^tBu_2$. This makes structure **I** impossible and, thus, might be anticipated to create an even more reactive species.[3,4] We are interested in detailed comparison of the synthesis, structure, and reactivity to those of the monodentate P^tBu_2Me analogue.

Experimental Section

General. All manipulations were carried out with standard Schlenk and glovebox techniques under purified argon. Benzene, toluene, and pentane were dried over sodium benzophenone ketyl, distilled, and stored in gastight solvent bulbs. Benzene-d_6 and toluene-d_8 were dried by appropriate methods and vacuum-distilled prior to use. Et_3SiH, $HC{\equiv}CPh$, and C_6HF_5 were purchased from Aldrich and used without further purification. Gaseous reagents were purchased from Air Products and used as received. $[Ru(H)_2(CO)_2(d^tbpe)]$ was synthesized as reported.[5] ^1H, ^{31}P, ^{19}F, and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer (^1H, 300 MHz; ^{31}P, 122 MHz; ^{19}F, 282 MHz; ^{13}C, 75 MHz) or on a Varian INOVA 400 spectrometer (^1H, 400 MHz; ^{31}P, 161 MHz; ^{19}F, 376 MHz; ^{13}C, 100 MHz). ^1H NMR chemical shifts are reported in parts per million downfield of tetramethylsilane with use of residual solvent resonances as internal standards. ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4. ^{19}F NMR chemical shifts are externally referenced to CF_3COOH/C_6D_6. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. UV−vis spectra were recorded on a HP 8452A UV−vis and a Perkin-Elmer Lambda 19 UV−vis/near-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer at Indiana University. All calculations were carried out with the Gaussian 94 package of programs[6] at the DFT(B3PW91),[7] MP2,[8] and CCSD(T)[9] levels. Effective core potentials were used for replacing the 28 innermost

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[*] Authors to whom correspondence should be addressed. E-mail: caulton@indiana.edu and eisenste@lsd.univ-montp2.fr.

[†] Université de Montpellier.

[‡] Indiana University.

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Table 1. Crystallographic Data for $[\mathrm{Ru(CO)_2(^tBu_2PCH_2CH_2P^tBu_2)}]_2$

formula	$\mathrm{C_{40}H_{80}O_4P_4Ru_2}$	space group	$P2_1/c$
a, Å	11.353(2)	T, °C	−168
b, Å	18.453(4)	λ, Å	0.71069
c, Å	11.830(2)	ρ_{calcd}, g/cm^{-3}	1.384
β, deg	112.92(1)	μ(Mo Kα), cm^{-1}	8.4
V, Å^3	2282.81	R^a	0.0669
Z	2	$R_w{}^b$	0.0376
fw	951.11		

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

electrons of Ru[10] and 10 innermost electrons of P.[11] A basis set was of valence double-ζ quality[10−12] with polarization functions on all atoms.[13,14]

$[\mathrm{Ru(CO)_2(d^tbpe)}]_2$. A 100-mL solvent seal flask was charged with a yellow solution of $[\mathrm{Ru(H)_2(CO)_2(d^tbpe)}]$ (190 mg, 0.4 mmol) in benzene (15 mL). The solution was frozen at −78 °C, the headspace was evacuated, and the flask was filled with $\mathrm{C_2H_4}$ (1 atm). The sealed flask was heated to 55 °C (**CAUTION!**) with vigorous stirring for 6 h, and the gas atmosphere was changed every 2 h. The resulting orange solution was evaporated to dryness, giving a dark green residue, which was recrystallized from toluene/pentane (1:5) at −40 °C, yielding dark green crystals. Yield: 80 mg (43%). Anal. Calcd for $\mathrm{C_{40}H_{80}O_4P_4Ru_2}$: C, 50.51; H, 8.48. Found: C, 50.90; H, 8.31. IR ($\mathrm{C_6D_6}$, cm^{-1}): 1944, 1873 ν(CO); (Nujol, cm^{-1}) 1869, 1668 ν(CO). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.15 (d, 36 H, CH_3), 1.36 (d, 4 H, CH_2). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$) δ 23.42 (t, P−C), 30.64 (t, CH$_3$), 36.65 (t, CH$_2$), 208.73 (dd, CO, J(CP$_{\mathrm{trans}}$) = 72 Hz, J(CP$_{\mathrm{cis}}$) = 18 Hz). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 99 (s). UV−vis ($\mathrm{C_6H_6}$): 424 nm (ϵ = 4260 L mol^{-1} cm^{-1}), 672 nm (ϵ = 2455 L mol^{-1} cm^{-1}).

X-ray Diffraction Structure Determination of $[\mathrm{Ru(CO)_2(^tBu_2PC_2H_4P^tBu_2)}]_2$. A typical green crystal was selected, affixed to a glass fiber using silicone grease, and then rapidly transferred to the goniostat and cooled to −168 °C. A systematic search of a limited hemisphere of reciprocal space was used to determine that the crystal possessed monoclinic symmetry and systematic absences corresponding to the unique space group $P2_1/c$ (Table 1). Subsequent solution and refinement confirmed this choice. The data were collected (6° < 2θ < 50°) using a standard moving crystal−moving detector technique with fixed backgrounds at each extreme of the scan. Data were corrected for Lorentz and polarization effects and equivalent reflections averaged after correction for absorption. The structure, which consists of a dimer located at a center of inversion, was solved with some difficulty using direct methods (SHELX) and Fourier techniques. Hydrogen atoms were readily located in a difference Fourier phased on the non-hydrogen atoms. Since several of the hydrogen atoms tended to converge to negative isotropic thermal parameters upon refinement, only their positions were varied in the final cycles of refinement. A final difference Fourier was featureless, the largest peak of intensity 0.55 e/Å^3, lying adjacent to the Ru atom.

General Procedure for the Reaction of $[\mathrm{Ru(CO)_2(d^tbpe)}]$ with $\mathrm{C_2H_4}$, $\mathrm{H_2}$, CO, and HCl. An NMR tube fitted with a Teflon stopcock was filled with a green solution of $[\mathrm{Ru(CO)_2(d^tbpe)}]$. The solution was frozen, the headspace was evacuated, and 1 atm of the corresponding gas (except HCl) was admitted, giving a yellow solution in the time of mixing.

$[\mathrm{Ru(C_2H_4)(CO)_2(d^tbpe)}]$ was obtained from $[\mathrm{Ru(CO)_2(d^tbpe)}]_2$ (4.6 mg, 0.005 mmol) and $\mathrm{C_2H_4}$ (1 atm). $\mathrm{C_7D_8}$ IR ($\mathrm{C_7D_8}$, cm^{-1}): 1964, 1892 ν(CO). ^{1}H NMR ($\mathrm{C_7D_8}$, 293 K) δ 1.14 (d, 36 H, CH_3), 1.35 (d, 4 H, CH_2), 2.10 (br, 4 H, C$_2H_4$). ^{1}H NMR ($\mathrm{C_7D_8}$, 208 K): δ 0.82, 1.23 (br, 40 H, CH_3, CH_2), 1.83, 2.15, 2.34, 2.49 (s, each 1 H, C$_2H_4$). ^{13}C{^{1}H} NMR ($\mathrm{C_7D_8}$, 208 K): δ 23.80 (m, P−C), 29.91 (m, CH$_3$, C_2H$_4$), 37.04 (m, CH$_2$), 208.24 (dd, CO, J(CP$_{\mathrm{trans}}$) = 87 Hz, J(CP$_{\mathrm{cis}}$) = 15 Hz), 213.80 (m, CO). ^{31}P{^{1}H} NMR ($\mathrm{C_7D_8}$, 208 K): δ 105.18 (d, J(PP) = 19 Hz), 86.41 (d, J(PP) = 19 Hz).

$[\mathrm{Ru(H)_2(CO)_2(d^tbpe)}]$ was obtained from $[\mathrm{Ru(CO)_2(d^tbpe)}]_2$ (5.0 mg, 0.0052 mmol), $\mathrm{C_6D_6}$, and $\mathrm{H_2}$. ^{1}H and ^{31}P NMR spectra showed complete conversion to $[\mathrm{Ru(H)_2(CO)_2(d^tbpe)}]$, for which independent synthesis was reported elsewhere.[5]

$[\mathrm{Ru(CO)_3(d^tbpe)}]$ was obtained from $[\mathrm{Ru(CO)_2(d^tbpe)}]_2$ (3.9 mg, 0.0040 mmol), $\mathrm{C_6D_6}$, and CO. ^{1}H, ^{31}P NMR, and IR spectra showed complete conversion to $[\mathrm{Ru(CO)_3(d^tbpe)}]$, for which independent synthesis was reported elsewhere.[5]

$[\mathrm{RuHCl(CO)_2(d^tbpe)}]$ was obtained from $[\mathrm{Ru(CO)_2(d^tbpe)}]_2$ (4.5 mg, 0.0047 mmol), $\mathrm{C_6D_6}$, and HCl (0.0094 mmol). ^{1}H and ^{31}P NMR spectra showed complete conversion to $[\mathrm{RuHCl(CO)_2(d^tbpe)}]$, for which independent synthesis was reported elsewhere.[5]

$[\mathrm{RuH(C{\equiv}CH)(CO)_2(d^tbpe)}]$. An NMR tube fitted with a Teflon stopcock was filled with a green solution of $[\mathrm{Ru(CO)_2(d^tbpe)}]_2$ (8.1 mg, 0.0084 mmol) in $\mathrm{C_6D_6}$ (0.5 mL). The solution was frozen, the headspace was evacuated, and 1 atm of $\mathrm{C_2H_2}$ was admitted, giving a yellow solution in the time of mixing. The solution was filtered, and the filtrate was evaporated to dryness, giving a yellow solid. Yield: 6.0 mg (71%). IR ($\mathrm{C_6H_6}$, cm^{-1}): 2031, 1989 (νCO). ^{1}H NMR ($\mathrm{C_6D_6}$): δ −7.21 (dd, 1 H, RuH, J(HP) = 21 Hz, 25 Hz), 0.97−1.47 (m, 40 H, CH_3, CH_2), 1.35 (s, 1 H, CH). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 23.29 (m, PC), 23.90 (m, PC), 29.66−30.83 (m, CH$_3$), 36.07−36.56 (m, CH$_2$), 71.84 (s, CH), 96.66 (d, RuCC, J(CP) = 20 Hz), 201.13, 202.10 (CO, multiplicity of the signal is not given, due to the weakness of the signal). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 108.03 (d, J(PP) = 13 Hz), 97.79 (d, J(PP) = 13 Hz). Elemental analysis was not obtained due to the close similarity to the phenyl analogue, below.

$[\mathrm{RuH(C{\equiv}CPh)(CO)_2(d^tbpe)}]$. In an NMR tube, HCCPh (1.55 μL, 0.014 mmol) was added to a green solution of $[\mathrm{Ru(CO)_2(d^tbpe)}]_2$ (7.0 mg, 0.0074 mmol) in $\mathrm{C_6D_6}$ (0.5 mL), yielding a yellow solution in the time of mixing. The solution was filtered, and the filtrate was evaporated to dryness, giving a yellow solid. Yield: 3.0 mg (35%). Anal. Calcd for $\mathrm{C_{28}H_{46}O_2P_2Ru}$: C, 58.22; H, 8.03. Found: C, 58.20; H, 8.07. IR ($\mathrm{C_6H_6}$, cm^{-1}): 2108 (νC≡C), 2027, 1989 (νCO). ^{1}H NMR ($\mathrm{C_6D_6}$): δ −7.20 (dd, 1 H, RuH, J(HP) = 21, 26 Hz), 0.91−1.36 (m, 40 H, CH_3, CH_2), 6.90 (t, 1 H, C$_6H_5$), 7.10 (t, 2 H, C$_6H_5$), 7.65 (d, 2 H, C$_6H_5$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 23.35 (m, PC), 23.87 (m, PC), 29.66−30.64 (m, CH$_3$), 35.98−36.50 (m, CH$_2$), 112.03 (d, RuCC, J(CP) = 20 Hz), 124.35, 127.20, 127.60, 128.12, 131.59 (s, CPh, C(aryl)), 200.98, 202.04 (CO, multiplicity of the signal is not given, due to the weakness of the signal). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 107.74 (d, J(PP) = 13 Hz), 97.14 (d, J(PP) = 13 Hz).

$[\mathrm{RuH(FBF_3)(CO)_2(d^tbpe)}]$. In an NMR tube, $\mathrm{HBF_4}$ (2.0 μL, 0.012 mmol, 85% in $\mathrm{Et_2O}$) was added to a green solution of $[\mathrm{Ru(CO)_2(d^tbpe)}]_2$ (5.6 mg, 0.0059 mmol) in $\mathrm{C_7D_8}$ (0.5 mL), yielding a bright orange solution in the time of mixing. ^{1}H and ^{31}P NMR spectra showed complete conversion to $[\mathrm{RuH(FBF_3)(CO)_2(d^tbpe)}]$, for which independent synthesis was reported elsewhere.[5]

$[\mathrm{RuH(SiEt_3)(CO)_2(d^tbpe)}]$. In an NMR tube, $\mathrm{HSiEt_3}$ (1.7 μ, 0.011 mmol) was added to a green solution of $[\mathrm{Ru(CO)_2(d^tbpe)}]_2$ (5.2 mg, 0.0055 mmol) in $\mathrm{C_7D_8}$ (0.5 mL), yielding a yellow solution in the time of mixing. IR ($\mathrm{C_7D_8}$, cm^{-1}): 1995, 1954 (νCO), 1908 (νRuH). ^{1}H NMR ($\mathrm{C_7D_8}$, 333 K): δ 1.13 (d, 36 H, CH_3), 1.29 (d, 4 H, CH_2). ^{1}H NMR ($\mathrm{C_7D_8}$, 213 K): δ −8.09 (dd, 1 H, RuH, J(HP) = 21 Hz, 23 Hz), 0.40−1.80 (m, 55 H, CH_3, CH_2). ^{31}P{^{1}H} NMR ($\mathrm{C_7D_8}$, 333 K): δ 102.60 (s). ^{31}P{^{1}H} NMR ($\mathrm{C_7D_8}$, 213 K): δ 100.99 (d, J(PP) = 15 Hz), 100.05 (d, J(PP) = 15 Hz).

$[\mathrm{RuH(C_6F_5)(CO)_2(d^tbpe)}]$. A green solution of $[\mathrm{Ru(CO)_2(d^tbpe)}]_2$ (6.1 mg, 0.0064 mmol) in $\mathrm{C_6HF_5}$ (0.5 mL) was heated for 4 h at 80 °C, yielding a bright yellow solution. All volatiles were removed in a vacuum, and the white residue was dried for 12 h in vacuo. IR ($\mathrm{C_7D_8}$, cm^{-1}): 1997, 1941 ν(CO). ^{1}H NMR ($\mathrm{C_7D_8}$) δ −6.89 (dt, 1 H, RuH, J(HF) = 29 Hz, J(HP) = 25 Hz), 0.76−1.70 (m, 40 H, CH_3, CH_2). ^{31}P{^{1}H} NMR ($\mathrm{C_7D_8}$): δ 89.37 (d, J(PP) = 11 Hz), 109.99 (m). ^{19}F NMR ($\mathrm{C_7D_8}$): −165.47 (m, *m*-F), −165.06 (m, *m*-F), −164.01 (m, *p*-F), −100.39 (m, *o*-F), −96.80 (m, *o*-F). The fluorine content frustrated satisfactory combustion analysis.

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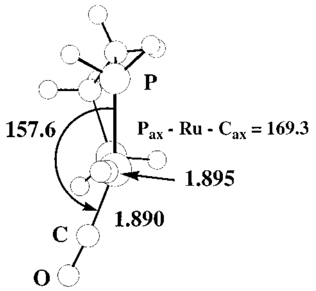
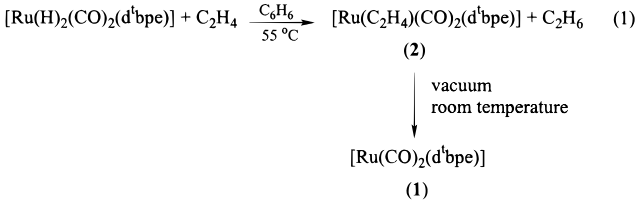


Figure 1. DFT calculated structure of $Ru(CO)_2(H_2PCH_2CH_2PH_2)$.

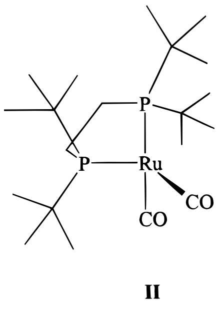
Results

Preparation and Characterization of $[Ru(CO)_2(d^tbpe)]$ (1) (d^tbpe = $^tBu_2PCH_2CH_2P^tBu_2$). Reaction of $[Ru(H)_2(CO)_2(d^tbpe)]$ with C_2H_4 gave the yellow ethylene complex $[Ru(C_2H_4)(CO)_2(d^tbpe)]$ (**2**). The ethylene ligand in **2** is labile and can be easily removed in a vacuum, yielding dark green $[Ru(CO)_2(d^tbpe)]$ (**1**) (eq 1).



$$\begin{tikzcd}[Ru(H)_2(CO)_2(d^tbpe)] + C_2H_4 \arrow[r, "C_6H_6", "55\ ^\circ C"'] & {[Ru(C_2H_4)(CO)_2(d^tbpe)] + C_2H_6\ (\mathbf{2})} \arrow[d, "\text{vacuum, room temperature}"] \\ & {[Ru(CO)_2(d^tbpe)]\ (\mathbf{1})}\end{tikzcd} \quad (1)$$

The ^1H NMR spectrum of **1** shows one doublet for the four ^{t}Bu substituents of the chelate ligand, the $^{31}P\{^1H\}$ NMR shows one singlet, and the $^{13}C\{^1H\}$ NMR spectrum exhibits one doublet of doublets for the CO ligands. These spectroscopic data are *consistent* with a square-planar structure of **1** in solution. In particular the two *J*(PC) values in the CO NMR signal have magnitudes consistent with one being to a trans P (72 Hz) and one being to a cis P (18 Hz). Furthermore, the CO ligands show two absorption bands in the IR spectrum in hexane (1944 and 1873 cm^{-1}). From the intensities of these, a C−Ru−C angle of 84° was calculated.[15] However, quantum calculations (see below) show that **1** has a structure **II** which differs subtly from square-planar.



II

Computational Study of *cis*-$Ru(PR_3)_2(CO)_2$. The structure of the model complex *cis*-$Ru(CO)_2(H_2PCH_2CH_2PH_2)$, **1**, was fully optimized without any symmetry constraint with DFT-(B3PW91) calculations. The resulting structure (Figure 1) shows the preference for a nonplanar geometry with two different CO ligands (P−Ru−C = 169.3° and 157.6° and equal CO bond lengths of 1.159 Å). The angle between the two CO ligands (91.6°) is in very close agreement with that calculated from the IR measurement. The five-membered ring has the expected envelope shape. Despite the absence of ^{t}Bu substituents on P, the calculated structure seems to mimic well the experimental system. We believe that no agostic interaction is present in this complex in part because the constraint of the five-membered ring prevents the Ru−P−C (^{t}Bu) angle from achieving the small angle (∼100°) characteristic of agostic donation.

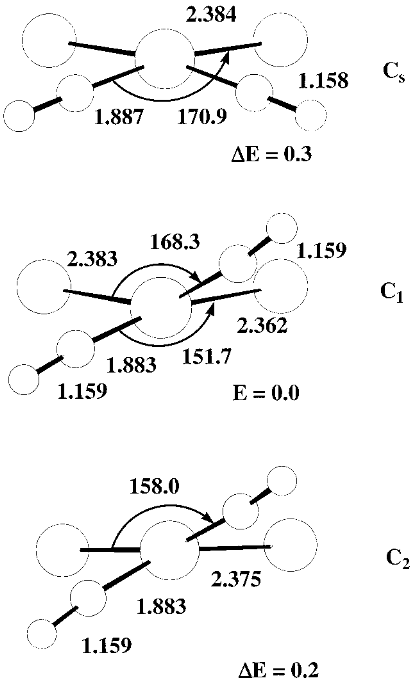


Figure 2. DFT calculated structure for *cis*-$Ru(CO)_2(PH_3)_2$ (hydrogens omitted) showing the ground state (center) and two transition states (C_s and C_2) for site exchange of carbonyls and of phosphines.

In order to determine how the chelate ligand influences the coordination at the Ru center, we also optimized the geometry of *cis*-$Ru(CO)_2(PH_3)_2$ in its singlet and triplet states. The triplet state is calculated to be 26.1 kcal·mol^{-1} above the singlet minimum, proving without doubt the preference for a diamagnetic species. This is consistent with the experimental NMR evidence for diamagnetism. For the singlet state, the geometrical structure is found to be very similar to that of the chelate phosphine system (P−Ru−C = 151.7° and 168.3°, C−Ru−C = 90.3°, CO = 1.158 Å) (Figure 2 (center)). In particular, the two CO ligands are also not equivalent (C_1 symmetry). The nonplanar coordination and the lack of symmetry elements (C_s or C_2) is thus an intrinsic property of the ground state of the *cis*-$Ru(CO)_2(PH_3)_2$ system. The compound *trans*-$Ru(CO)_2(PH_3)_2$ is calculated to be 1.3 kcal·mol^{-1} more stable than *cis*-$Ru(CO)_2(PH_3)_2$.

While the two isomers (*trans*- and *cis*-$Ru(CO)_2(PH_3)_2$) are nonplanar, they show significant differences. The C−Ru−C angle (138.8°) of the trans isomer is significantly smaller than any trans L−Ru−L′ angle in the cis isomer. In contrast, the P−Ru−P angle (171.0°) is larger than any P−Ru−P angle in the cis isomer. In addition, the Ru−C−O angle is bent (168.4°), while no such distortion is obtained in the cis isomer (Ru−C−O = 173.3°, 176.0°). The geometry of a d^8 ML_4 complex is thus highly sensitive to the nature[16] and site occupancy[1] of the π acceptor ligands.

How can this conclusion of inequivalent carbonyls (and thus inequivalent ^{31}P nuclei) be reconciled with the NMR spectra? Two nonplanar singlet transition states for equivalencing the two CO and the two PH_3 ligands were located (Figure 2) only 0.2 and 0.3 kcal·mol^{-1} above the minimum. The introduction

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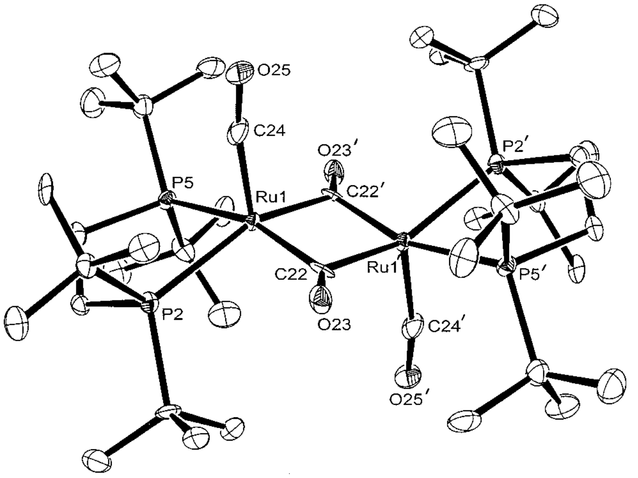

Figure 3. ORTEP drawing of the non-hydrogen atoms of centrosymmetric $[Ru(CO)_2({}^tBu_2PC_2H_4P^tBu_2)]_2$ in the solid state.

Table 2. Selected Bond Distances (Å) and Angles (deg) in **1**

Ru(1)−P(2)	2.4593(19)	Ru(1)−C(24)	1.836(7)
Ru(1)−P(5)	2.4620(19)	O(23)−C(22)	1.198(7)
Ru(1)−C(22)	2.016(7)	O(25)−C(24)	1.165(8)
Ru(1)−C(22)′	2.050(6)	Ru(1)−Ru(1)′	2.703
P(2)−Ru(1)−P(5)	83.99(6)	Ru(1)−P(2)−C(3)	106.29(23)
P(2)−Ru(1)−C(22)	154.08(18)	Ru(1)−P(2)−C(6)	116.11(22)
P(2)−Ru(1)−C(22)′	86.10(19)	Ru(1)−P(2)−C(10)	119.88(22)
P(2)−Ru(1)−C(24)	102.75(23)	Ru(1)−P(5)−C(4)	105.18(24)
P(5)−Ru(1)−C(22)	87.18(19)	Ru(1)−P(5)−C(14)	118.32(24)
P(5)−Ru(1)−C(22)	164.47(18)	Ru(1)−P(5)−C(18)	118.56(23)
P(5)−Ru(1)−C(24)	98.45(23)	Ru(1)−C(22)−Ru(1)	83.31(24)
C(22)−Ru(1)−C(22)′	96.69(24)	Ru(1)−C(22)−O(23)	139.9(5)
C(22)−Ru(1)−C(24)	102.6(3)	Ru(1)−C(22)′−O(23)′	136.6(5)
C(22)′−Ru(1)−C(24)	95.4(3)	Ru(1)−C(24)−O(25)	169.8(6)

of ZPE correction does not alter the relative energies of the C_1, C_2, and C_s structures, thus proving that the C_1 structure is a true minimum. Furthermore, the energy of the square-planar singlet structure, obtained from optimization under constraints, is only 0.7 kcal·mol^{-1} above the same minimum. The extreme flatness of this potential energy surface was also established by MP2 calculations, which find a difference in energy of 0.4 kcal·mol^{-1} between planar and nonplanar structures, in favor of a nonplanar structure. Finally, CCSD(T) calculations on MP2 geometries give a difference of energy of 0.3 kcal·mol^{-1}. Thus, quantum calculations all agree on a highly flexible structure for *cis*-$Ru(CO)_2(PH_3)_2$. The flatness of the surface indicated by all levels of calculations thus accounts for the NMR spectroscopic observation of two chemically equivalent CO and also of identical ^{t}Bu substituents on P, all by time averaging.

Solid-State Structure. Surprisingly, the solid-state structure of green crystalline **1** differs from the structure in solution. The X-ray structure analysis reveals that **1** has a centrosymmetric dimeric solid-state structure (Figure 3). The two ruthenium centers are bridged by two CO ligands. The Ru−Ru distance is 2.703 Å (Table 2). Each Ru center is surrounded by two P atoms, one terminal CO ligand, and two bridging CO ligands, giving a square-pyramidal geometry. The four apical-to-basal angles fall into the narrow range 95.4(3)°−102.75(23)°. The Ru−C (183.6(7) pm) and C−O distances (116.5(8) pm) of the terminal CO ligand are distinctly different from the corresponding distances of the bridging CO ligands (Ru−C, 201.6(7), 205.0(6) pm; C−O, 119.8(7) pm). The terminal CO ligand is slightly bent with a Ru−C−O angle of 169.8(6)°. The Ru−C−Ru angle of the bridging CO ligand is 83.31(24)°. The P−Ru−P angle is 83.99(6)°, which is comparable to the P−Ru−P angle in $[RuH(CO)_2(d^tbpe)]BAr^F_4$ (85.76(7)°).[5]

The dimeric solid-state structure of **1** is supported by the IR spectrum in Nujol mull, which shows one absorption for a terminal CO ligand (1869 cm^{-1}) and one band for a bridging CO ligand (1668 cm^{-1}). Further proof of the different structure of **1** in solution and the solid state comes from the UV−vis spectra in solution and in the solid state. While the solution spectrum (benzene) shows two bands at 424 and 672 nm, in which the latter one is responsible for the green color, the solid-state spectrum (Fluorolube) exhibits only one band (665 nm), supporting the different structure of **1** in solution and in the solid state. Furthermore, a possible interaction between coordinatively unsaturated monomeric **1** and the solvent could be excluded by comparison of the UV−vis spectra in benzene and *n*-hexanes, which are essentially identical. In order to exclude that traces of benzene cause the low but observable solubility and affect the UV−vis spectrum of **1** in *n*-hexanes, two samples of **1** were prepared in *n*-hexanes with identical concentrations but one sample containing a trace of benzene. The UV−vis spectra of these samples were essentially identical; in particular the intensities of the bands were identical, which shows that the solubility of **1** in *n*-hexanes is not caused by traces of benzene breaking up the dimeric structure of solid **1**.

In retrospect, the comment made earlier here that $Ru(CO)_2(d^tbpe)$ in solution is not planar may seem like splitting hairs. Despite the fact that all calculations suggest a preference for a nonplanar structure, the tiny difference in energy from the calculated planar structure does not allow a definitive decision for the experimental compound. On the other hand, this is a situation where, at the level of less than ∼3° or ∼0.02 Å, the uncertainty here is analogous to the question of FHF^- (centrosymmetric or not?),[17] $(OC)_5CrHCr(CO)_5^-$ (two equal Cr−H distances, or not?),[18] "stretched" H_2 complexes[19] (0.6 Å variation in $R_{H/H}$ alters energy by <1 kcal/mol), and (most contemporary) CH_5^+.[20] What is true of both $Ru(CO)_2(d^tbpe)$ and CH_5^+ is that *several* (inequivalent) *structures* are at energies comparable to kT at 25 °C. Thus, several nonplanar as well as the planar structures are populated at 25 °C, which merely describe it as an exceptionally deformable four-coordinate d^8 species (but compare $RhCl(CO)(P^tBu_3)_2$[21] and $Rh(PPh_2Me)_4^+$,[22] where steric effects are becoming acute). This structural "plasticity" can lead to atypical interaction (albeit weak interactions) with exceptionally weak donors (cf. $Ru(CO)_2(Me_2PC_2H_4PMe_2)$ in inert gas matrixes), as well as the dimerization observed here which can be completely destroyed by entropy at 25 °C and below ($T\Delta S$ ∼3 kcal/mol at, e.g., −60 °C).

Reactivity

Binding of C_2H_4 to $[Ru(CO)_2(d^tbpe)]$ (**1**) in arene solvents is complete in the time of mixing at 25 °C. The green color of **1** changes to yellow. The ethylene ligand in $[Ru(C_2H_4)(CO)_2(d^tbpe)]$ (**2**) is weakly bound. Heating a solution of **2** in benzene

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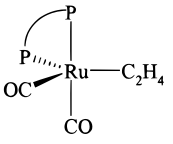
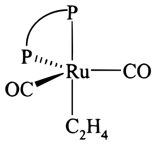
to 60 °C or removal of the ethylene atmosphere resulted in loss of the C_2H_4 ligand and formation of $[Ru(CO)_2(d^tbpe)]$ (**1**), indicated by the green color of the solution. $[Ru(C_2H_4)(CO)_2(d^tbpe)]$ (**2**) is rapidly fluxional. The ^1H NMR spectrum at 25 °C shows only one doublet for the ^tBu group, one doublet for the $(CH_2)_2$ bridge of the chelate ligand, and a broad signal for the ethylene ligand. The ethylene protons decoalesce to four chemical shifts at 208 K, which excludes structure **IV** under the conditions where olefin rotation has been halted. Four ethylene chemical shifts are consistent with structure **III**, regardless of the orientation of the C=C vector. Structure **III** is also supported by the low-temperature $^{13}C\{^1H\}$ NMR spectrum, which shows a doublet of doublets and a multiplet for the inequivalent CO ligands, and the $^{31}P\{^1H\}$ NMR spectrum, which shows two chemical shifts. The observation that only one CO has one large J(PC) (87 Hz) is only consistent with structure **III**. The IR spectrum in toluene exhibits two CO bands, whose intensities permit a C−Ru−C angle of 91° to be calculated. The ν_{CO} values rise by about 20 cm^{-1} on binding of C_2H_4 to **1**, which suggests that ethylene is more a π-acid than a donor in the adduct.



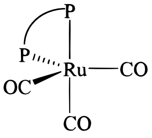
III



IV

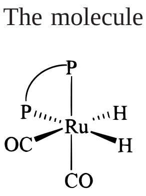
Other olefins, such as $H_2C{=}CHF$ and $H_2C{=}CHCH_3$, are also only weakly bound. The stability of the adducts decreases according to $H_2C{=}CH_2 > H_2C{=}CHF > H_2C{=}CHCH_3$. This order has been determined from the temperature dependence of the color change from orange ($[Ru(olefin)(CO)_2(d^tbpe)]$) to green ($[Ru(CO)_2(d^tbpe)]$). $[Ru(olefin)(CO)_2(d^tbpe)]$ loses $H_2C{=}CH_2$ at ca. 60 °C and $H_2C{=}CHF$ at 40 °C, and $H_2C{=}CHCH_3$ is already lost at room temperature.

Reaction with CO in benzene occurs in the time of mixing at 25 °C to give $[Ru(CO)_3(d^tbpe)]$, which has an IR spectrum (three ν_{CO} absorptions) consistent with structure **V**. NMR spectra at 25 °C and at −60 °C show only one $^{31}P\{^1H\}$ chemical shift, one ^tBu ^1H NMR chemical shift, and one triplet carbonyl signal in the $^{13}C\{^1H\}$ NMR, all consistent with a rapidly fluxional molecule.



V

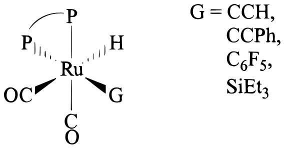
H_2 oxidatively adds in the time of mixing at 25 °C to give a product of structure **VI**. The molecule shows inequivalent ^{31}P nuclei, four ^tBu ^1H NMR chemical shifts, and two hydride chemical shifts, one with a large coupling to phosphorus. The fact that the hydrides are cis is consistent with a mechanism in which H_2 approaches perpendicular to the quasi-plane $RuP_2(CO)$ of **II**. The ^1H NMR spectrum of $[Ru(H)_2(CO)_2(d^tbpe)]$ recorded at 70 °C shows a small line broadening of the hydride signals while the ^{31}P NMR signals are unaffected. In no case was there evidence of thermal loss of H_2 by NMR spectroscopy or by a color change of a solution of $[Ru(H)_2(CO)_2(d^tbpe)]$ at elevated temperatures.



VI

The oxidative addition of HCl (gas) and HBF_4 (solution in Et_2O) gives *trans*-$[RuHCl(CO)_2(d^tbpe)]$ and *trans*-$[RuH(FBF_3)(CO)_2(d^tbpe)]$, respectively. The formation of the trans products indicates a nonconcerted mechanism for these reactions or a fast rearrangement of the kinetic cis product to the thermodynamically more stable trans product.

Reaction with HC≡CR (R = H, Ph) in the time of mixing changes the green color to yellow. A hydride signal proves that these products are formed by oxidative addition of one C−H bond, and its two different P/H coupling constants show the molecule to be stereochemically rigid, with inequivalent phosphines. The similarity of the two $^2J_{PH}$ values (21 and 25 Hz) is most consistent with structure **VII**, which is analogous to the oxidative addition product with H_2. The acetylide β-hydrogen is also detected when R = H.



VII

The green color of $[Ru(CO)_2(d^tbpe)]$ (**1**) transforms to yellow during 4 h at 80 °C in neat C_6F_5H. The product has structure **VII**, and the ^{19}F NMR spectrum shows five chemical shifts, showing that rotation around the $Ru-C_{(ipso)}$ bond is slow, due apparently to steric pressure from the two nearby ^tBu groups. Indeed, all compounds with isomeric form **VII** are probably favored because they put the bulkier ligand cis to only one P^tBu_2 group. The alternative placement of H and R creates cis interactions between R and both phosphorus donors.

The reaction of $[Ru(CO)_2(d^tbpe)]$ (**1**) with $HSiR_3$ (R = Me, Et) at 25 °C gave a bright yellow solution in the time of mixing. The ^1H NMR spectrum of this solution at 25 °C showed only a broad signal for the hydride and no signals for the alkyl groups of the silane. Heating the solution to 60 °C resulted in a green solution, indicative of equilibrium between the oxidative addition product $[RuH(SiR_3)(CO)_2(d^tbpe)]$ and $[Ru(CO)_2(d^tbpe)]$ (**1**) which can be shifted toward $[Ru(CO)_2(d^tbpe)]$ (**1**) by heating. The ^1H NMR spectrum at 60 °C was nearly identical to the spectrum of $[Ru(CO)_2(d^tbpe)]$ (**1**) at room temperature. However, a resolved ^1H NMR spectrum for $[RuH(SiR_3)(CO)_2(d^tbpe)]$ obtained at low temperatures showed the expected hydride doublet of doublets with nearly identical coupling constants for a hydrido ligand in a coordination sphere according to structure **VII**. The $^{31}P\{^1H\}$ NMR spectrum exhibits two doublets for the inequivalent P atoms in structure **VII**. These spectral features are comparable to those of $RuH(SiEt_3)(CO)_2(Me_2PCH_2CH_2PMe_2)$ (which is nonfluxional)[23] and to those of $FeH(SiR_3)(CO)_2(Ph_2PCH_2CH_2PPh_2)$,[24] which shows *intramolecular* fluxionality. Neither of these shows the dissociative process (loss of $H-SiR_3$) observed here for $RuH(SiR_3)(CO)_2(d^tbpe)$.

When N_2 was admitted to a solution of **1**, no reaction was observed at room temperature as judged by NMR spectroscopies

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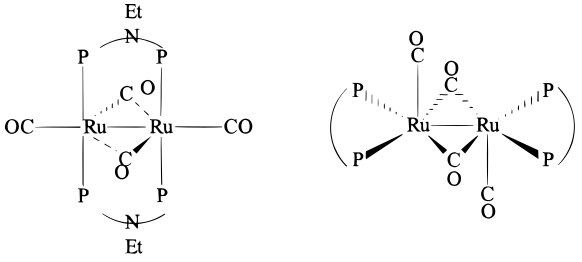
and by the absence of any color change. The ^{31}P chemical shift of **1** in THF is within 1 ppm of that in benzene, indicating no coordination of THF. Dissolving **1** in acetone-d_6 gave no reaction according to ^{1}H and ^{31}P NMR spectroscopy after 1 h at room temperature. A solution of **1** in THF is also stable against a large excess of H_2O for 20 h at room temperature, and CH_3OH in C_6D_6 does not react with **1** at 25 °C. All of these are consistent with **1** being a strong π-base and reductant, but not strongly Lewis acidic toward σ-bases.

Discussion

While Cp*Rh(CO)[25−27] and $Os(CO)_4$[28−30] are d^8 16-electron transient species which also dimerize, $Ru(CO)_2L_2$ is unique in doing so reversibly on change from solution to the solid state.

There are two distinct classes of compounds to which to compare the Ru/Ru distances in $[Ru(CO)_2L_2]_2$. In the unbridged dimer $[Ru(octaethylporphyrin)]_2$[31] and in $[Ru(tetraazaannulene)]_2$[32] the Ru^{II}/Ru^{II} distances are 2.408 and 2.379 Å, respectively. The 18-electron rule, their diamagnetism, and the absence of any bridging ligands collectively demand a Ru═Ru double bond in these species. However, these differ from $[Ru(CO)_2L_2]_2$ in that they are d^6/d^6 dimers and they represent square-*planar* RuN_4 species which become apically connected square pyramids when they dimerize. An authentic $(Ru^0)_2$ dimer is $[Ru(CO)_2\{(RO)_2PNEtP(OR)_2\}]_2$,[33] where the Ru/Ru distance is 2.73 Å (R = Me) or 2.76 Å (R = ^{i}Pr); this is also a case where the 18-electron rule demands a Ru═Ru double bond. In this dimer structure, each bidentate ligand bridges the two metals, in contrast to our chelate; while there are two bridging carbonyls in this dimer, they are highly asymmetric, with the long and short Ru−C distances differing by 0.33 Å (R = Me) and 0.51 Å (R = ^{i}Pr). Associated with this difference is a change in metal coordination geometry shown in Chart 1. In fact, neglecting the long (2.3−2.4 Å) Ru/C distance, the geometry around Ru in $[Ru(CO)_2\{(RO)_2PNEtP(OR)_2\}]_2$ rather closely mimics the nonplanar "saw-horse" geometry of $Ru(CO)_2(P^tBu_2Me)_2$.

Chart 1



1

Single and double Ru^0/Ru^0 bonds bridged by $(Ph_2P)_2CH_2$ ligands have distances of 2.784 and 2.697 Å, respectively.[34] The unbridged single Ru^I/Ru^I bond in $[Ru(CO)_3(dppe)]_2^{2+}$ has a distance of 3.04 Å.[35]

The dimerization of $[Ru(CO)_2(d^tbpe)]_2$ in the solid state stands also in contrast to the structure of the analogous $[Ru(CO)_2L_2]$ complexes of monodentate L, which are monomeric in the solid state and in solution. One reason for this different behavior is the more sterically compact cis P_2 geometry of $[Ru(CO)_2(d^tbpe)]_2$, which enables dimerization without excessive end-to-end inter-phosphine repulsions.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure of $[Ru(CO)_2(^tBu_2PCH_2CH_2P^tBu_2)]_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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