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Structure of Bis(dimethylphenylphosphine)(ethylene)(carbonyl)dichlororuthenium(II), $RuCl_2(CO)(C_2H_4)(P(CH_3)_2(C_6H_5))_2$, a Six-Coordinate d^6 Complex Containing Ethylene as a Ligand

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Bis(dimethylphenylphosphine)(ethylene)(carbonyl)dichlororuthenium(II), $RuCl_2(CO)(C_2H_4)(P(CH_3)_2(C_6H_5))_2$, is a six-coordinate complex containing ethylene as one of its ligands. In the solid state, the molecule has crystallographically imposed C_2-2 symmetry, the twofold axis being along the Cl(1)–Ru bond and bisecting the trans C_2H_4 group. The equatorial ligands of this octahedral complex are the PMe_2Ph groups, the Cl(2) atom, and the CO group. Owing to the imposed symmetry, the CO group is disordered with respect to the Cl(2) atom. Important distances are Ru–P = 2.414 (1), Ru–Cl(1) = 2.415 (2), Ru–Cl(2) = 2.454 (3), Ru–C(of C_2H_4) = 2.214 (4), Ru–C(of CO) = 1.831 (10), and C=C = 1.376 (10) Å. The disposition of the ethylene group is such that the C=C bond is essentially parallel to the Ru–P bonds. Spectroscopic data obtained from the compound in solution are consistent with this solid-state structure. However, in solution the ethylene group is rotating about the ruthenium–ethylene bond as evidenced by the single proton resonance observed for all four C_2H_4 protons even down to −40 °C. The compound crystallizes with four molecules in space group C_{2h}^6-$C2/c$ of the monoclinic system in a cell of dimensions a = 9.033 (4) Å, b = 11.494 (5) Å, c = 20.936 (9) Å, and β = 99.10 (2)°. The structure has been refined by least-squares methods to values of the R and weighted R indices of 0.044 and 0.055, respectively, for the 94 variables and 2998 significant observations.

Complexes of ruthenium(II) containing organic ligands have frequently been postulated as intermediates in reactions catalyzed by or involving ruthenium compounds. We have been preparing organoruthenium(II) complexes which we hoped might act as suitable model compounds for these proposed intermediates and have recently published details of the preparation and reactions of alkyl, phenyl, and acyl complexes.[2,3] Olefin complexes have also been proposed as intermediates in such reactions (notably in catalytic hydroformylation,[4] hydrogenation,[5,6] isomerization,[7] and dimerization[8] of olefins and in decarbonylation of aldehydes[9]). With this in mind we attempted, successfully, to prepare an ethylene complex of ruthenium(II). To the best of our knowledge, no six-coordinate complex containing ethylene as one of its ligands (and indeed, no ethylene complex of a d^6 metal ion) has ever been studied by X-ray crystallography. We therefore decided to determine the structure of the compound $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$ (Me = methyl, Ph = phenyl).

Experimental Section

The complex $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$ was prepared by passing ethylene through a solution of *trans*-$RuCl_2(CO)_2(PMe_2Ph)_2$[10] in chloroform. Crystals for the structure determination were grown by slow evaporation of a solution of the crude product in a mixture of dichloromethane and petroleum ether (bp 80–100 °C) under an atmosphere of ethylene. The complex slowly loses ethylene in solution but is stable over long periods in the solid state. Spectroscopic data for this compound were obtained on Varian A60A NMR, JEOL FX60 NMR, and Perkin-Elmer 257 grating IR[10] spectrometers. NMR data, measured in $CDCl_3$ solution, with chemical shifts in δ (ppm downfield from Me_4Si) follow (resonances associated with the phenyl groups are omitted). ^1H NMR: 2.13, t, 6 (P*Me*$_2$Ph); 2.14, t, 6 (P*Me*$_2$Ph); 2.27, t, 4 (C_2H_4). ^{13}C NMR: 11.6, t (P*Me*$_2$Ph); 13.6, t (P*Me*$_2$Ph); 58.6, s (C_2H_4); 194.0, t (CO).

Preliminary film data from a single crystal mounted in air revealed Laue symmetry $2/m$ and systematic absences characteristic of space groups C_{2h}^6-$C2/c$ and C_s^4-Cc of the monoclinic system. On the basis of the setting angles of 12 manually centered reflections (28° < 2θ(Mo Kα_1) < 35°), the cell constants given in Table I were obtained. Data were collected at room temperature on a Picker FACS-I diffractometer using methods general in this laboratory.[11] Important features of data collection are given in Table I.

The processed data were corrected for absorption effects and then Friedel pairs were compared. The excellence of their agreement is strong evidence that the correct space group is the centrosymmetric one, $C2/c$. This was assumed in ensuing calculations. With four molecules in space group $C2/c$, symmetry 2 is imposed crystallographically on the molecules. The structure was solved in a straightforward way, using procedures and computer programs described before.[11] From a sharpened, origin-removed Patterson function, the positions of the Ru, Cl(1), and P atoms were obtained. Other nonhydrogen atoms were found in a subsequent Fourier map. The overall stereochemistry was apparent: the twofold axis is coincident with the Ru–Cl(1) bond, bisects the trans C_2H_4 groups, and results in disorder of the Cl(2) atom with the CO group. However, it has proved possible to refine atoms Cl(2), C(1), and O(1) anisotropically, presumably because these atoms are reasonably well-separated (minimum approach is 0.66 Å). The final cycle of least-squares refinement included anisotropic vibration for all nonhydrogen atoms with the exception of the six carbon atoms of the phenyl group which was treated as a rigid group with each atom vibrating isotropically. Also varied were the positions and isotropic thermal parameters of the two independent hydrogen atoms of the ethylene group. The fixed contributions from the other hydrogen atoms

Table I. Crystal Data and Data Collection Procedures for $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$

compound	$RuCl_2(CO)(C_2H_4)(P(CH_3)_2(C_6H_5))_2$
formula	$C_{19}H_{26}Cl_2OP_2Ru$
mol wt	504.34
a	9.033 (4) Å
b	11.494 (5) Å
c	20.936 (9) Å
β	99.10 (2)°
V	2146.1 Å^3
Z	4
space group	C_{2h}^6-$C2/c$
imposed symmetry	2
ρ_{calcd}	1.560 g/cm^3
ρ_{obsd}	1.53 (2) g/cm^3
bounding planes	$\{\bar{1}01\}$, $\{010\}$, $\{001\}$
crystal vol	0.032 mm^3
linear absorption coeff (Mo Kα)	11.19 cm^{-1}
transmission factors	0.685–0.811
takeoff angle	3.0°
aperture	5.2 mm wide by 4.4 mm high; 32 cm from crystal
scan range	0.9° below Mo Kα_1 peak to 1.0° above Mo Kα_2 peak
scan speed	2.0° 2θ/min
collection range	$\pm h, k, +l$, 5° ≤ 2θ(Mo Kα_1) ≤ 63°; $\pm h, k, -l$, 5° ≤ 2θ(Mo Kα_1) ≤ 30°
no. of data	4303 total; 3485 (including Friedel pairs) with $F_o^2 > 3\sigma(F_o^2)$; 2998 (unique in $C2/c$) with $F_o^2 > 3\sigma(F_o^2)$ (p = 0.04)

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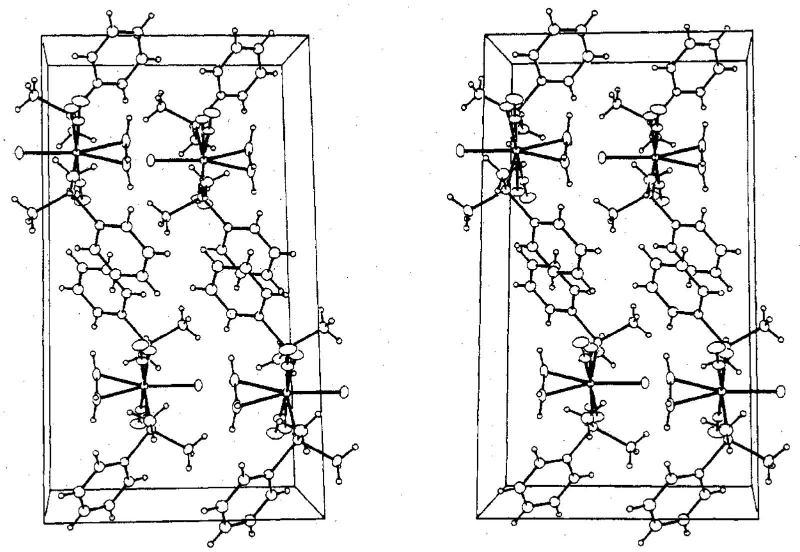

Figure 1. Stereoview of the unit cell of $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$. The 20% probability ellipsoids of thermal motion are shown, except for the hydrogen atoms which have been made artificially small. Molecular disorder, engendered by a crystallographically imposed twofold axis, is shown. The view is down *x*, with *y* going from left to right.

Table II. Idealized Hydrogen Positions for the PMe_2Ph Group

atom	*x*	*y*	*z*
H1C(12)	0.284	0.316	0.124
H1C(13)	0.235	0.444	0.036
H1C(14)	0.028	0.412	−0.045
H1C(15)	−0.131	0.253	−0.038
H1C(16)	−0.082	0.125	0.050
H1C(3)	0.375	0.056	0.222
H2C(3)	0.397	0.104	0.154
H3C(3)	0.369	0.189	0.209
H1C(4)	0.022	−0.051	0.105
H2C(4)	0.177	−0.032	0.084
H3C(4)	0.166	−0.095	0.149

(Table II) were computed using a C–H distance of 0.95 Å and normal geometry. The thermal parameters were fixed at $B(H) = B(C) + 1$ Å^2. The final refinement converged to values of R and R_w of 0.044 and 0.055 and to an error in an observation of unit weight of 1.64 electrons for the 94 variables and 2998 observations. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices indicated no unusual trends. Only two of those reflections omitted from the refinement because $F_o^2 < 3\sigma(F_o^2)$ had $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$. The highest peak on a final difference Fourier map has a height of 1.2 (1) e/Å^3 and is associated with the rigid group.

Final positional and thermal parameters are tabulated in Tables III and IV. Root-mean-square amplitudes of vibration are given in Table V.[12] In Table VI the values of $10|F_o|$ vs. $10|F_c|$ for the reflections

Table III. Positional and Thermal Parameters for the Nongroup Atoms of $RuCl_2(CO)(C_2H_4)(P(CH_3)_2(C_6H_5))_2$

ATOM	X[A]	Y	Z	B11[B] OR B,A^2	B22	B33	B12	B13	B23
RU	0	0.125717(28)	1/4	68.94(40)	40.82(24)	14.87(8)	0	-4.11(12)	0
CL(1)	0	-0.08439(12)	1/4	303.0(36)	45.09(84)	33.22(45)	0	41.8(11)	0
CL(2)	0.22400(30)	0.11065(29)	0.33286(13)	94.2(32)	136.0(29)	18.52(56)	-3.6(22)	-9.3(10)	0.75(96)
P	0.143950(92)	0.105257(70)	0.162821(41)	84.84(97)	51.82(61)	18.16(19)	2.95(57)	1.00(33)	-1.22(26)
O(1)	0.27975(83)	0.14455(81)	0.34503(38)	99.3(95)	194.(11)	24.2(18)	-13.7(77)	-10.6(33)	-11.3(35)
C(1)	0.1723(11)	0.13587(79)	0.30899(42)	113.(11)	97.0(79)	15.6(17)	-4.2(75)	1.1(35)	1.9(31)
C(2)	0.03961(90)	0.30884(36)	0.22451(33)	314.(13)	44.1(27)	43.5(19)	-5.7(47)	72.3(42)	-0.3(18)
C(3)	0.34386(41)	0.11506(37)	0.18974(20)	89.9(41)	108.5(40)	24.51(93)	19.9(33)	0.7(16)	2.6(16)
C(4)	0.12660(51)	-0.03364(32)	0.12036(20)	191.9(70)	59.3(28)	26.4(11)	7.0(35)	17.9(22)	-7.7(14)
H(21)	0.1293(66)	0.3130(54)	0.2306(28)	7.6(19)					
H(22)	-0.0168(73)	0.3225(56)	0.1772(34)	9.9(21)					

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

Table IV. Parameters for the Group Atoms of $RuCl_2(CO)(C_2H_4)(P(CH_3)_2(C_6H_5))_2$

ATOM	X	Y	Z	B,A^2	ATOM	X	Y	Z	B,A^2
C(11)	0.10665(25)	0.20710(18)	0.095232(95)	3.04(5)	C(14)	0.04810(31)	0.35964(20)	-0.00939(11)	4.58(8)
C(12)	0.20050(23)	0.30228(21)	0.09109(10)	3.91(7)	C(15)	-0.04574(24)	0.26446(22)	-0.00524(10)	4.51(8)
C(13)	0.17122(29)	0.37855(18)	0.03878(13)	4.81(8)	C(16)	-0.01647(24)	0.18819(18)	0.04706(12)	3.86(7)

RIGID GROUP PARAMETERS

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
PHENYL	0.07738(19)	0.28337(14)	0.042923(79)	2.1664(15)	2.8857(14)	2.2462(16)

[A] X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

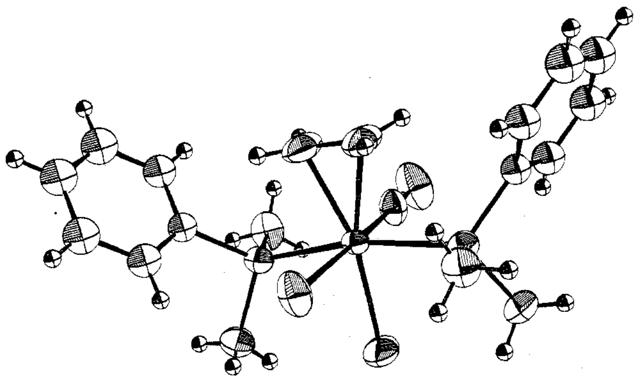

Figure 2. The $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$ molecule. The 50% probability ellipsoids of thermal motion are shown, except for the hydrogen atoms. The molecular disorder is not shown.

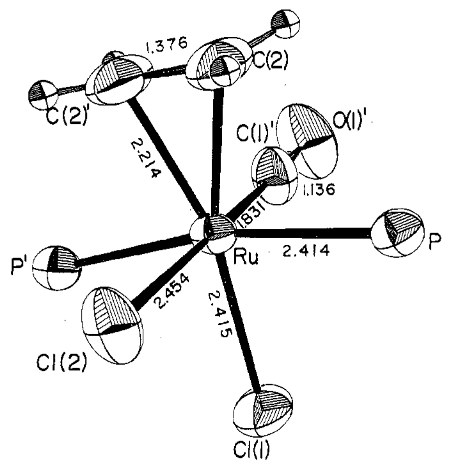

Figure 3. The inner coordination sphere of the $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$ molecule, showing the labeling scheme and principal distances. The orientation is the same as that of Figure 2. The 50% probability ellipsoids are shown. The disorder of atom Cl(2) with the CO group is not shown. A primed atom is related to the corresponding unprimed atom by the crystallographically imposed twofold axis.

used in the refinement are given.[12]

Results and Discussion

The crystal structure of $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$ consists of well-separated molecules. The closest calculated H···H interaction is 2.50 Å. A packing diagram is shown in Figure 1. Disordering of the Cl(2) atom with the CO group is displayed in that figure.

The overall molecular structure is shown in Figure 2, while Figure 3 displays, in the same orientation, the inner coordination sphere along with the labeling scheme and some important distances. Additional distances and angles are given in Table VII, along with associated standard deviations as estimated from the inverse matrix.

There has been considerable use of metal–chlorine bonds as indicators of the trans-bond weakening effect of ligands in octahedral complexes of d^6 metal ions. Lupin and Shaw[13] showed that in a range of ruthenium(II) complexes the Ru–Cl stretching frequency varies according to the ligand trans to the chloro ligand as follows:

trans ligand	ν_{Ru-Cl}, cm^{-1}
Cl^-	347-299
CO	311-266
PR_3	262-229

This was taken to indicate that the trans effect of CO is slightly greater than that of Cl^- but that the effect of a phosphorus ligand is significantly greater than either. It should be possible to use the Ru–Cl bond length as an alternative indicator for the effect. Unfortunately, most of the octahedral ruthenium(II) complexes which have been studied have terminal chloro ligands as mutually trans pairs. In such compounds,[14-20] the Ru–Cl bond length varies between 2.391 and 2.446 Å. As expected, the length of the bond to the chloro ligand trans to PEt_2Ph in *mer*-$[RuCl_3(PEt_2Ph)_3]^-$ (2.513 Å) lies outside this range.[15] Our finding that the length of the bond to the chloro ligand trans to CO in $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$ is 2.454 Å fits in nicely, giving the same order of Cl^- < CO < PR_3 for the trans-bond weakening effect as that proposed by Lupin and Shaw.[13] The value is also fairly close to that (2.428 Å) reported[21] for the length of the bond to the chloro ligand trans to CO in $RuCl_2(CO)(CSe)(PPh_3)_2$.

Table VII. Selected Distances (Å) and Angles (deg) in $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$

	Distances		
Ru-P	2.414 (1)	C(2)-C(2)'[a]	1.376 (10)
Ru-Cl(1)	2.415 (2)	C(2)-H(21)	0.80 (6)
Ru-Cl(2)	2.454 (3)	C(2)-H(22)	1.05 (7)
Ru-C(1)	1.831 (10)	P-C(3)	1.808 (4)
Ru-C(2)	2.214 (4)	P-C(4)	1.822 (4)
C(1)-O(1)	1.136 (10)	P-C(11)	1.826 (2)
	Angles		
P-Ru-P'	168.8 (4)	Cl(2)-Ru-C(2)'	92.5 (2)
P-Ru-Cl(1)	84.4 (2)	C(2)-Ru-C(2)'	36.2 (3)
P-Ru-Cl(2)	92.6 (7)	C(2)-Ru-C(1)	87.1 (4)
P-Ru-Cl(2)'	86.6 (7)	C(2)-Ru-C(1)'	85.9 (4)
P-Ru-C(1)	89.9 (2)	Ru-C(1)-O(1)	178.5 (8)
P-Ru-C(1)'	90.8 (3)	H(21)-C(2)-H(22)	118 (5)
P-Ru-C(2)	77.5 (13)	C(3)-P-C(4)	102.2 (2)
P-Ru-C(2)'	113.7 (13)	C(3)-P-C(11)	104.7 (2)
Cl(1)-Ru-Cl(2)	86.0 (8)	C(4)-P-C(11)	101.1 (2)
Cl(1)-Ru-C(1)	93.7 (3)	C(3)-P-Ru	112.9 (1)
Cl(1)-Ru-C(2)	161.9 (13)	C(4)-P-Ru	116.4 (1)
Cl(2)-Ru-C(1)'	177.4 (3)	C(11)-P-Ru	117.9 (1)
Cl(2)-Ru-C(2)	95.2 (2)		
C(2)-H(21)-H(22) } C(2)'-H(21)'-H(22)' }	24 (11) α[b]	C(2)'-C(2) } Ru-P }	5.8 (2)
		C(2)'-C(2)-Ru-P	−178.6 (8)
C(2)-C(2)' } C(2)-H(21)-H(22) }	78 (6) β[b]		

[a] Primed atoms are related to unprimed atoms by the twofold axis. [b] See text.

More unexpected, however, is the sizable difference between the Ru–Cl bond length (2.458 (1) Å) in the 1,5-cyclooctadiene complex $RuCl_2(C_8H_{12})(NH_2C_6H_{13})_2$, where each chloro ligand is trans to a double bond in the diene,[20] and that (2.415 (2) Å) to the chloro ligand trans to ethylene in $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$. Admittedly the difference is smaller than that between the extreme ends of the range given above for Ru–Cl bonds trans to chloro ligands, and the comparison is between diolefin and monoolefin complexes (though the diolefin is not conjugated, but simply has two isolated double bonds joined by saturated organic linkages); even so, given the overall similarity in the geometries of the two complexes, the difference in Ru–Cl bond lengths seems large.

The nature of the ethylene ligand is of obvious interest in the present structure, since this is the first structural determination of a six-coordinate complex containing ethylene. In discussing olefin complexes it is convenient[22] to consider C=C bond lengths, M–C bond lengths, nonplanarity of the bound olefin, and disposition of the olefin with respect to the other ligands. An extended discussion of the coordination of olefins to transition metals has been presented recently[22] and will not be repeated here. The C=C bond length of 1.376 (10) Å in the present compound lies within the normal range. Values between 1.354 (15) Å in $K[PtCl_3(C_2H_4)]$[23] and 1.46 (2) Å in $Ni[P(O\text{-}o\text{-}tol)_3]_2(C_2H_4)$[24] have been reported. Owing to the relatively small range of C═C distances in the bound C_2H_4 ligand and to the large uncertainties in the determinations of these distances, little can be learned from such values. There is, of course, the expected lengthening over the distance of 1.337 Å in free ethylene. The Ru–C(ethylene) distance of 2.214 (4) Å in the present complex is at the extreme of the tabulated range.[22] This is expected, since the present complex has a higher coordination number than the other compounds. Nonplanarity of bound olefins is most conveniently assessed by the values of the angles α and β, where in the present instance α is the angle between the normals to the two CH_2 planes and β is the angle the C═C vector makes with the normal to the CH_2 plane.[22] If the ethylene group were planar, then α would be 0° and β would be 90°. The present values of 24 (11)° and 78 (6)° for α and β indicate that the ethylene ligand possibly is nonplanar, with the H atoms bent away from the metal.

The orientation of the C═C bond with respect to the other ligands is a feature of particular interest in the present six-coordinate structure. Generally, the C═C bond lies in the trigonal plane in three-coordinate complexes, is perpendicular to the plane in square-planar complexes, and is in the equatorial plane in trigonal-bipyramidal complexes.[22] Such orientations result from electronic rather than steric effects. In the present structure the C═C bond is closely within one of the equatorial planes of the octahedron, rather than being skewed, and this effect is again electronic as there are no unusual intramolecular contacts. That the C═C bond is closely parallel to the Ru–P bonds is illustrated by the angle between C(2)–C(2)′ and Ru–P of 5.8 (2)° and by the torsion angle C(2)′–C(2)–Ru–P of −178.6 (8)°. The orientation of the ethylene group may perhaps be rationalized in the following way. Among the ligands about the Ru atom, the ethylene and carbonyl are the good π acceptors. If the ethylene ligand lay in the same plane as the carbonyl group, then these ligands would compete for a d orbital for π-bonding purposes. With the ethylene ligand nearly parallel to the Ru–P bonds, and hence essentially perpendicular to the Ru–C–O linkage, it interacts with a d orbital which is not suitably positioned to interact with the CO ligand.

Facile rotation of the olefin about the metal–olefin bond has been observed for a number of compounds in solution.[25-28] That the complex has the same general arrangement of ligands in solution as in the solid state was established by ^1H and ^{13}C NMR spectroscopy. Interestingly, a single resonance is observed for all four protons in the ethylene ligand: that this is caused by rotation about the ruthenium–ethylene bond rather than by rapid reversible dissociation of the ethylene ligand is established by the fact that the resonance is split into a 1:2:1 triplet by coupling to the two phosphorus nuclei. Attempts to determine whether the rate of rotation could be slowed down sufficiently by cooling to obtain a limiting low-temperature spectrum [as has been done for ethylene complexes of lower coordination number of rhodium(I),[25,26] osmium(0),[27] and platinum(II)[28]] were rather unsuccessful. In some solvents the ethylene proton resonance at ambient temperature is very close to those from the methyl protons of the PMe_2Ph ligands and moves behind them as the temperature is lowered, making it difficult to detect changes in appearance. However, we did establish that in dichloromethane solution rotation is still rapid on the NMR time scale at −40 °C. This evidence of a low-energy barrier to rotation is particularly interesting in view of the relatively high coordination number of the complex. One other point of note in the NMR spectra of the complex is that the resonance for the carbon atoms of the ethylene ligands, unlike that for the ethylene protons, shows no discernible splitting by the phosphorus nuclei.

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Registry No. $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$, 67225-39-2; *trans*-$RuCl_2(CO)_2(PMe_2Ph)_2$, 17141-04-7.

Supplementary Material Available: Root-mean-square amplitudes of vibration (Table V) and a listing of structure amplitudes (Table VI) (22 pages). Ordering information is given on any current masthead page.

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