(ClO_4) (XXVIII), both *E* and *Z* isomers are present in almost equal amounts (*E*:*Z* = 8:7).

The occurrence of different isomers in the complexes under consideration can be attributed to the restricted rotation of the N=C bond. In addition, one may consider several other factors: (1) The isomers may result from the mode of attack by, for example, the alcohol on the coordinated nitrile, that is, one side or the other. (2) Inversion may occur at the coordinated nitrogen site. (3) The rotation about the Ni-N bond may be contributing to the isomeric distribution. Factor 1 seems to be unlikely, because there is no obvious reason for preferential attack on a particular side. The possibility of factor (2) cannot be ruled out, although such inversion at the nitrogen center is without precedence in imino-ether, amidine, and imidate complexes. Factor 3 might play an important role, as hindered rotation of the nitrogen-metal bond has been reported in some imino-ether[7] and amidine[13] complexes. The dynamics of internal rotation in the present complexes could not be investigated due to the already mentioned solubility problem.

Acknowledgment. We are grateful to Professor U. R. Ghatak and Dr. R. V. Venkateswaran of the Department of Organic Chemistry of this institute, and the sophisticated instruments facility at the Indian Institute of Science, Bangalore, for recording ^1H NMR spectra.

Supplementary Material Available: Listings of analytical data (Table I), infrared and visible spectral data (Table II), and ^1H NMR for the principal ligand moiety in the imino-ether and amidine complexes (Table III) (3 pages). Ordering information is given on any current masthead page.

Contribution from the Cattedra di Chimica Industriale, Dipartimento di Chimica Organica, Università di Firenze, I-50121 Firenze, Italy, and Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy

Interaction between $Ru(CO)_2(CH_3COO)_2[P(n\text{-}Bu)_3]_2$ and $Ru_4(CO)_8(CH_3COO)_4[P(n\text{-}Bu)_3]_2$ in Solution: Synthesis and Characterization of $[P(n\text{-}Bu)_3](CO)_2Ru(\mu\text{-}OH)(\mu\text{-}CH_3COO\text{-}O)(\mu\text{-}CH_3COO\text{-}O,O')Ru(CO)(CH_3COO)[P(n\text{-}Bu)_3]$

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The title compound, obtained by reaction of $Ru(CO)_2(CH_3COO)_2[P(n\text{-}Bu)_3]_2$ with $Ru_4(CO)_8(CH_3COO)_4[P(n\text{-}Bu)_3]_2$ at 120 °C in *n*-heptane solution, has been characterized by standard analytical procedures, IR and NMR spectrometry, and X-ray diffraction. The formation of intermediates such as $Ru(CO)_2(CH_3COO\text{-}O,O')(CH_3COO)[P(n\text{-}Bu)_3]$ is suggested, and the reactivity of the system is discussed. Crystal data for the title compound $C_{33}H_{64}O_{10}P_2Ru_2$: space group *Pbca*, $a = 32.473$ (10) Å, $b = 15.342$ (5) Å, $c = 17.401$ (6) Å, $V = 8669$ (5) Å^3, $Z = 8$, $D_{calcd} = 1.356$ g cm^{-3}, $F(000) = 3680$, Mo Kα_1 radiation, $\lambda = 0.709300$ Å for the determination of lattice parameters. The structure, determined by Patterson and Fourier methods and refined by least squares to $R_F(4193/546) = 0.0697$, consists of neutral complex molecules in which two octahedral metal centers are joined together by three oxygen bridges: μ-hydroxo [Ru-O = 2.071 (6), 2.104 (6) Å; Ru-O-Ru = 104.2 (2)°], μ-acetato-*O* [Ru-O = 2.147 (6), 2.196 (6) Å; Ru-O-Ru = 98.6 (3)°], and μ-acetato-*O,O'* [Ru-O = 2.102 (6), 2.065 (7) Å, Ru-O-C = 132.3 (6), 128.2 (6)°], with an intermetallic contact Ru···Ru = 3.294 (2) Å. Coordination is completed to octahedral by a phosphorus atom of a phosphine [Ru-P = 2.316 (3) Å] and two carbonyls [Ru-C = 1.890 (8) Å, average] about one ruthenium atom and by a phosphorus atom [Ru-P = 2.262 (3) Å] of the second phosphine, one carbonyl [Ru-C = 1.823 (11) Å], and one oxygen [Ru-O = 2.092 (7) Å] of a terminal monodentate acetate group about the second ruthenium atom. The two octahedra share the O[μ-hydroxo]···O[μ-acetato-*O*] edge, and the angular deformations in them are roughly symmetrical with respect to this edge.

Introduction

In the hydrogenation of carboxylic acids, carried out in the presence of phosphine-substituted ruthenium carbonyls, the evolving catalytic system gives rise to the formation of phosphine-substituted ruthenium carbonyl carboxylates.[1,2] Complexes such as $Ru(CO)_2(CH_3COO)_2[P(n\text{-}Bu)_3]_2$ (I), $Ru_2(CO)_4(CH_3COO)_2[P(n\text{-}Bu)_3]_2$ (II), and $Ru_4(CO)_8(CH_3COO)_4[P(n\text{-}Bu)_3]_2$ (III) have been detected in the crude mixture of the acetic acid hydrogenation by using $H_4Ru_4(CO)_8[P(n\text{-}Bu)_3]_4$ as catalytic precursor.

In order to understand the role of these compounds in the hydrogenation process, we studied the reactivity of ruthenium carbonyl carboxylates under comparable reaction conditions, in particular the interaction between I and III. The reaction was monitored by infrared spectroscopy using an IR pressure cell with heating facilities.

The constitution and structure of the new dinuclear product IV obtained in this reaction has been unequivocally defined by X-ray crystal structure analysis.

Table I. IR and ^1H NMR Data for $Ru_2(CO)_3(CH_3COO)_3(OH)[P(n\text{-}Bu)_3]_2$ (IV)

IR,[a] cm^{-1}	ν_{CO}	2060 (s), 1991 (vs), 1942 (vs), 1900 (vw)
	ν_{COO}	1678 (m), 1592 (m), 1561 (m), 1470 (w), 1425 (mw)
	others	1392 (mw), 1360 (w), 1338 (w), 1271 (m)
^1H NMR,[b] δ		0.80-1.15 (t, 18 H, CH_3CH_2), 1.15-2.05 (m, 36 H, $-CH_2CH_2CH_2P$), 1.82 (s, 3 H, CH_3COO), 1.88 (s, 3 H, CH_3COO-*O*), 2.37 (s, 3 H, CH_3COO-*O,O'*), 7.34 (s, 1 H, OH)

[a] C_6D_{12} as solvent. [b] Tetramethylsilane was used as internal standard, CD_2Cl_2 as solvent.

Results

(a) Spectroscopic Analyses. In the 0-50 °C temperature range a reversible interaction between I and III has been observed in *n*-heptane solution.[3] Above 50 °C, this system reacts, giving rise

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0020-1669/87/1326-1592$01.50/0

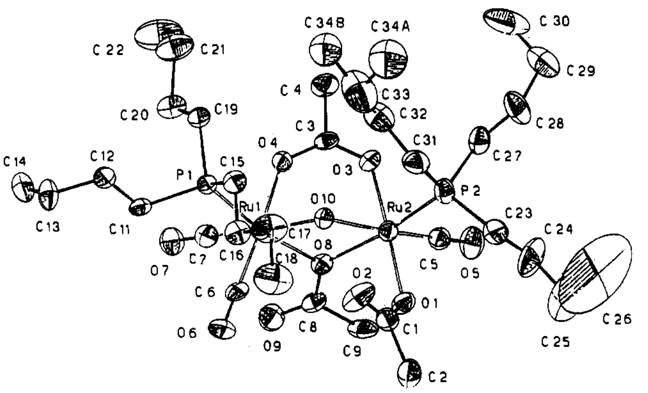
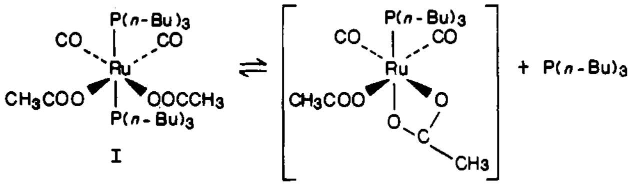


Figure 1. ORTEP drawing of a molecule of IV (ellipsoids at 30% probability).

Scheme I



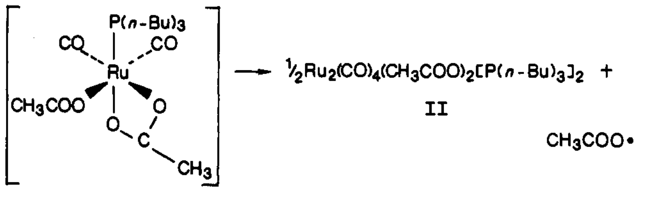
I

VII

Scheme II

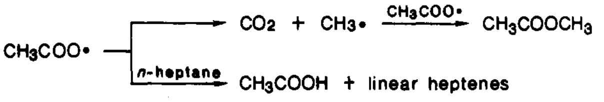
$$\underset{\text{III}}{Ru_4(CO)_8(CH_3COO)_4[P(n\text{-}Bu)_3]_2} + 2P(n\text{-}Bu)_3 \longrightarrow \underset{\text{II}}{2Ru_2(CO)_4(CH_3COO)_2[P(n\text{-}Bu)_3]_2}$$

Scheme III



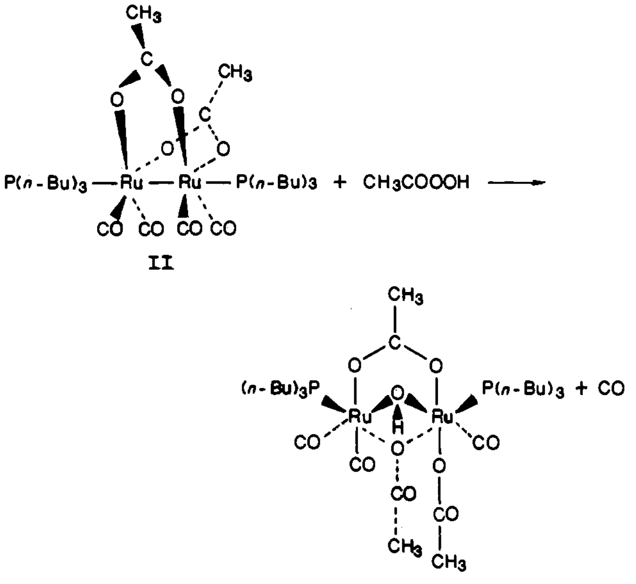
VII

Scheme IV



$$CH_3COO\bullet \longrightarrow CO_2 + CH_3\bullet \xrightarrow{CH_3COO\bullet} CH_3COOCH_3$$
$$CH_3COO\bullet \xrightarrow{n\text{-heptane}} CH_3COOH + \text{linear heptenes}$$

Scheme V



II

IV

to II and other unidentified intermediates. At 120 °C, the new product IV is present, characterized by absorption bands in the IR spectrum at 2056 (s), 1991 (vs), 1943 (vs), 1678 (m), 1590 (m), and 1561 (m) cm^{-1}. When the system is heated to higher temperatures (140 °C), it is completely transformed into II.

Complex IV cannot easily be isolated from the reaction solution, due to its high solubility. However, when the reaction is performed with a concentrated *n*-heptane solution in a sealed tube, IV is obtained as a pale yellow crystalline solid by slow evaporation of the solvent. At 120 °C II and IV exist in a molar ratio of 1:10 in the reaction medium.

According to the magnetic susceptibility, IV is diamagnetic. The IR spectrum of IV in C_6D_{12} solution shows a set of bands between 2060 and 1900 cm^{-1} due to the carbonyl stretching modes and another one between 1678 and 1425 cm^{-1} attributable to carboxylato stretching modes.[4,5] Full IR and ^{1}H NMR data are reported in Table I.

(b) Crystal Structure Analysis. The atomic coordinates and the equivalent isotropic thermal parameters of IV are quoted in Table II. Near the end of the refinement, a peak was found near the O10 oxygen atom, indicating that an hydroxo group was bridging the two metal atoms, in agreement with the NMR spectrum. Further refinement, carried out anisotropically for the non-hydrogen atoms, with the hydrogens (excepting those of the C26 and C34 methyls, not introduced) kept at the calculated positions (methyl and methylene groups as rigid groups with geometrical constraints: C–H = 1.08 Å; H–C–H = 109.5°) with thermal parameters for riding motions on covalently bonded atoms, slightly improved the results, giving a reasonable location of that hydrogen. Some disorder of the terminal parts of the *n*-butyl chains was indicated by exceptionally high values of the anisotropic thermal parameters of these atoms (Table II and Figure 1). C34 was split into two positions with 0.56 (5) and 0.46 (5) occupancy factors, while C33, C25–C26, C22, and C30 were considered as strongly anisotropic. This disorder is responsible for preventing further improvement.

Discussion

(a) Reactivity of the System. At room temperature I may, through its monodentate acetato ligands, react with other compounds by increasing the ligand coordination mode.[3] The IR spectra showing absorption bands characteristic of II before and after the formation of IV, above 120 °C, suggest the sequence of reactions reported below (Schemes I–III). Complex I in the presence of a "phosphine acceptor", such as III (Scheme I), loses a phosphine ligand and rearranges with chelation of one of the acetato ligands. Species VII thus formed has both a monodentate and a bidentate acetato ligand bound to a Ru(II) coordination center. Complexes of this type have already been described.[6,7]

The phosphine available (Scheme I) reacts with III to give II (Scheme II).

We have not been able to isolate species VII, which is probably very reactive and easily loses an acetato ligand to produce II (Scheme III).

At temperatures in the range of 60–100 °C, the IR absorptions observed in addition to those of II could be assigned to species VII.

The formation of acetic acid, methyl acetate, and linear heptenes in the reaction medium at temperatures above 120 °C may be

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Table II. Fractional Atomic Coordinates ($\times 10^4$) for Non-Hydrogen Atoms

atom	x/a	y/b	z/c	B_{eq},[a] Å^2
Ru1	567.3 (2)	1674.8 (5)	1808.1 (4)	3.43 (2)
Ru2	1561.0 (3)	2038.4 (6)	2013.2 (5)	3.81 (2)
P1	218 (1)	399 (2)	2095 (2)	3.86 (8)
P2	2066 (1)	1122 (2)	2402 (2)	4.83 (9)
O1	1754 (2)	2016 (5)	866 (4)	4.8 (2)
O2	1512 (3)	711 (6)	507 (5)	7.6 (3)
O3	1357 (2)	2077 (4)	3137 (4)	4.4 (2)
O4	670 (2)	1858 (4)	2990 (4)	4.4 (2)
O5	2111 (3)	3540 (6)	2383 (5)	7.4 (3)
O6	373 (3)	1420 (5)	127 (4)	6.5 (3)
O7	−228 (2)	2699 (5)	1893 (5)	6.3 (3)
O8	998 (2)	2721 (4)	1656 (4)	4.0 (2)
O9	560 (3)	3593 (5)	1042 (5)	6.6 (3)
O10	1129 (2)	1036 (4)	1845 (3)	3.6 (2)
C1	1699 (4)	1391 (9)	389 (7)	4.9 (4)
C2	1909 (4)	1537 (8)	−365 (6)	5.8 (4)
C3	1000 (4)	1967 (6)	3384 (6)	4.1 (3)
C4	932 (4)	1951 (9)	4264 (6)	5.9 (4)
C5	1895 (3)	2960 (8)	2233 (6)	4.7 (4)
C6	450 (3)	1506 (6)	750 (7)	4.4 (3)
C7	79 (4)	2331 (7)	1894 (7)	4.9 (4)
C8	906 (4)	3425 (7)	1266 (6)	4.3 (4)
C9	1274 (4)	4020 (7)	1084 (7)	5.6 (4)
C11	−287 (3)	264 (7)	1618 (6)	4.1 (3)
C12	−522 (3)	−569 (7)	1825 (7)	5.3 (4)
C13	−962 (4)	−589 (9)	1493 (9)	6.4 (5)
C14	−1234 (4)	120 (10)	1812 (9)	7.7 (6)
C15	525 (3)	−565 (6)	1852 (6)	4.7 (3)
C16	604 (4)	−690 (8)	987 (7)	5.5 (4)
C17	916 (5)	−1399 (9)	856 (8)	8.5 (6)
C18	1009 (6)	−1523 (11)	8 (9)	9.3 (7)
C19	116 (3)	254 (7)	3108 (6)	4.9 (4)
C20	−177 (4)	904 (9)	3439 (6)	6.4 (5)
C21	−201 (6)	782 (10)	4337 (8)	9.0 (7)
C22	−388 (8)	1431 (14)	4748 (10)	13.4 (11)
C23	2514 (4)	1026 (9)	1769 (8)	7.4 (5)
C24	2753 (5)	1889 (13)	1629 (12)	10.8 (8)
C25	3117 (10)	1855 (21)	1011 (17)	17.1 (14)
C26	3371 (15)	1426 (27)	1198 (40)	19.9 (39)
C27	2272 (3)	1407 (8)	3343 (7)	5.6 (4)
C28	2612 (4)	803 (11)	3679 (8)	7.8 (6)
C29	2751 (5)	1065 (13)	4509 (9)	8.8 (7)
C30	2436 (7)	941 (15)	5072 (10)	13.1 (10)
C31	1916 (4)	−5 (8)	2470 (8)	6.2 (4)
C32	1603 (5)	−219 (8)	3101 (9)	7.3 (6)
C33	1517 (12)	−1219 (13)	3110 (17)	13.2 (11)
C34A	1726 (13)	−1722 (28)	3480 (22)	9.8 (17)
C34B	1269 (15)	−1410 (33)	3635 (26)	9.6 (17)

[a] $B_{eq} = {}^8/_3\pi^2\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$.

tentatively attributed to reactions of the acetato radical postulated in Scheme III. It is in fact known that an acetato radical $CH_3COO^\bullet$ behaves as reported in Scheme IV.[8]

Compound IV may be formed from II according to Scheme V. Peracetic acid, possible source of the OH group present in the molecule of IV, may reasonably be thought to be formed according to

$$CH_3COO^\bullet + CH_3COOH \rightarrow CH_3COOOH + CH_3CO^\bullet$$

At higher temperatures II is again the main complex present.

(b) Description of the Structure. The complex is a neutral molecule consisting of two octahedral metal centers joined together by three oxygen bridges: μ-hydroxo, μ-acetato-*O* and μ-acetato-*O,O'*, as shown in Figure 1. The coordination polyhedra of the two metal atoms are distorted with respect to the regular octahedral arrangement, not only because of the difference of the ligands but also mainly as a consequence of the angular deformation imposed by the μ-hydroxo and μ-acetato-*O* bridges, which form O–Ru–O angles much smaller than the octahedral one (Table III). The two octahedra share the O8···O10 edge, and the angular deformations in them are roughly symmetrical with respect to this edge, the largest ones being the increase in the C7–Ru1–O8 = 99.1 (4)° and C5–Ru2–O8 = 100.6 (4)° angles, caused by the mentioned decreases. The mutual orientation of the two octahedra is defined by the dihedral angle (O4,O10,C6,C7) $\wedge$ (O3,O10,O1,C5) = 106.0 (2)° and by the angles O4···O10···O3 = 47.4 (8)°, C6···O10···O1 = 91.1 (9)°, and Ru1–O8–Ru2 = 98.6 (3)°.

The two coordination polyhedra differ because the sixth coordination site of Ru1 is occupied by a carbonyl, while at the corresponding position of Ru2 there is an oxygen of a terminal monodentate acetate group. Considering the coordination distances quoted in Table III, it appears that if exception is made for the μ-hydroxo and the μ-acetato-*O* groups for which the situation is inverted, all the other ligands coordinate to Ru1 at distances longer than those formed by the corresponding ligands to Ru2 and all the differences are quite significant. This fact does not seem to have a simple explanation except that of the different environment of the two metal atoms: the longer Ru–P and Ru–CO distances are observed at Ru1 where the strong π-acceptor CO occupies the position corresponding to that occupied by the terminal acetato ligand at Ru2.

The two Ru–O distances in the μ-hydroxo bridge are significantly different, the longer one [2.104 (6) Å] being a little shorter than those [2.142 (2), 2.144 (2), 2.134 (3) Å] found in $[Ru_2(\mu\text{-}OH)_3(PMe_3)_6]BF_4$ (V)[10] and [2.112 (2), 2.124 (2), 2.124 (2), 2.130 (2) Å] in $FeRu_2(\mu\text{-}OH)_2(CO)_8(PPh_3)_2$ (VI).[11] The angle Ru1–O10–Ru2 = 104.2 (2)° is larger than those [89.0 (2), 89.5 (2)°] found in V and those [91.05 (8), 91.23 (8)°] found in VI; these angles are to be compared with the Ru1···Ru2 distance, which is larger [3.294 (2) Å] in our compound than in V, where it is 3.004 (1) Å, and in VI, where the two metal atoms are 3.032 (1) Å apart. Considering also the Ru1–O10–H10 = 106 (5)° and Ru2–O10–H10 = 107 (5)° angles, it appears that there is a tendency to a tetrahedral environment for the μ-OH group, with the hydrogen atom involved in hydrogen bonding directed toward the uncoordinated oxygen, O2, of the terminal acetato group.

The metal···metal distance, which is indicative of a fairly weak interaction, is also related to the 18.7 (2)° bending of the Ru1–O8–Ru2–O10 ring along the O8···O10 direction. The other two six-membered coordination rings, C3,O3,Ru2,O10,Ru1,O4 and C3,O3,Ru2,O8,Ru1,O4, are both puckered (total puckering amplitudes[12] Q = 0.984 (4) and 1.041 (10) Å, respectively), and their conformations are half-chair with a local pseudomirror along C3,O8,O10.

Two carbonyl ligands are trans to the μ-hydroxo oxygen, each with respect to a ruthenium atom, while the two oxygen atoms of the μ-acetato-*O,O'* group are trans, one to a carbonyl with respect to Ru1 and the other to the terminal acetato group bound to Ru2.

All the acetato groups are planar and, in the case of the *O,O'*-bridging group, have C–O distances not significantly different [1.282 (13) and 1.250 (14) Å] and intermediary between the values for the longer [1.312 (5) Å] and the shorter [1.233 (5) Å] bonds usually found in carboxylic acids and esters, while in the other two groups these distances correspond quite well to the longer bond [1.309 (13) and 1.281 (14) Å] when the oxygen atom coordinates to metal, and to the shorter bond [1.216 (15) and 1.224 (15) Å] when oxygen is not involved in coordination.

As indicated by the torsion angles quoted in Table III, the two metal atoms lie nearly in the planes of the two bridging acetato groups, while the terminal acetato ligand is nearly coplanar with the O1,C5,O3,O10 coordination plane of Ru2, its orientation being determined by the previously mentioned O10–H···O2 hydrogen

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Table III. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg)

			Coordination Polyhedra				
Ru1–P1	2.316 (3)	Ru2–P2	2.262 (3)	Ru1–O4	2.102 (6)	Ru2–O3	2.065 (7)
Ru1–O10	2.071 (6)	Ru2–O10	2.104 (6)	Ru1–C6	1.898 (12)	Ru2–C5	1.823 (11)
Ru1–O8	2.147 (6)	Ru2–O8	2.196 (6)	Ru1–C7	1.884 (11)	Ru2–O1	2.092 (7)
O8–Ru1–O10	77.6 (2)	O8–Ru2–O10	75.8 (2)	O4–Ru1–C7	89.1 (4)	O3–Ru2–C5	88.2 (4)
C7–Ru1–O8	99.1 (4)	C5–Ru2–O8	100.6 (4)	C7–Ru1–C6	88.9 (5)	C5–Ru2–O1	92.0 (4)
O4–Ru1–O8	85.3 (2)	O3–Ru2–O8	89.3 (2)	C6–Ru1–O10	98.2 (4)	O1–Ru2–O10	93.2 (3)
C6–Ru1–O8	96.5 (4)	O1–Ru2–O8	89.2 (3)	P1–Ru1–O8	167.9 (2)	P2–Ru2–O8	169.6 (2)
P1–Ru1–O10	91.4 (2)	P2–Ru2–O10	94.0 (2)	O10–Ru1–C7	172.4 (4)	O10–Ru2–C5	173.6 (4)
P1–Ru1–O4	88.8 (2)	P2–Ru2–O3	88.1 (2)	O4–Ru1–C6	177.5 (4)	O3–Ru2–O1	178.6 (3)
P1–Ru1–C7	91.3 (4)	P2–Ru2–C5	89.3 (4)	Ru1–O10–Ru2	104.2 (2)	Ru1–O8–Ru2	98.6 (3)
P1–Ru1–C6	87.7 (3)	P2–Ru2–O1	93.3 (2)	Ru1–O8–C8	122.1 (7)	Ru2–O8–C8	136.9 (7)
O10–Ru1–O4	83.8 (2)	O10–Ru2–O3	86.5 (2)	Ru1–O4–C3	132.3 (6)	Ru2–O3–C3	128.2 (6)
						Ru2–O1–C1	126.1 (7)
			Acetato Groups				
C1–O1	1.281 (14)	O1–C1–O2	126.7 (11)	C8–O8	1.309 (13)	O8–C8–O9	123.5 (10)
C1–O2	1.224 (15)	O1–C1–C2	113.1 (10)	C8–O9	1.216 (15)	O8–C8–C9	114.8 (10)
C1–C2	1.495 (16)	O2–C1–C2	120.1 (11)	C8–C9	1.536 (17)	O9–C8–C9	121.7 (10)
C3–O3	1.250 (14)	O3–C3–O4	127.6 (9)				
C3–O4	1.282 (13)	O3–C3–C4	118.2 (10)				
C3–C4	1.548 (14)	O4–C3–C4	114.2 (10)				
			Carbonyls				
C5–O5	1.161 (14)	Ru2–C5–O5	179.0 (10)	C7–O7	1.145 (14)	Ru1–C7–O7	174.6 (10)
C6–O6	1.121 (14)	Ru1–C6–O6	178.4 (9)				
			Phosphines				
P1–C11	1.852 (10)	P2–C23	1.830 (14)	Ru1–P1–C11	115.6 (3)	Ru2–P2–C23	116.5 (5)
P1–C15	1.831 (10)	P2–C27	1.822 (12)	Ru1–P1–C15	111.5 (4)	Ru2–P2–C27	112.7 (4)
P1–C19	1.807 (10)	P2–C31	1.802 (12)	Ru1–P1–C19	113.9 (4)	Ru2–P2–C31	114.9 (4)
P1–C11–C12	115.4 (7)	P2–C23–C24	115.0 (11)	C11–P1–C15	106.7 (5)	C23–P2–C27	105.5 (6)
P1–C15–C16	114.7 (7)	P2–C27–C28	117.2 (9)	C11–P1–C19	105.0 (5)	C23–P2–C31	100.2 (6)
P1–C19–C20	114.4 (8)	P2–C31–C32	115.6 (9)	C15–P1–C19	103.1 (5)	C27–P2–C31	105.6 (6)
		C–C av	1.526 (11) [1.549 (11)]	C–C–C av	112.4 (7)^a		
			Torsion Angles				
Ru1–O4–C3–C4	–172.1 (6)			Ru2–O3–C3–C4	174.9 (7)		
Ru1–O8–C8–C9	–168.7 (7)			Ru2–O8–C8–C9	167.9 (8)		
				Ru2–O1–C1–C2	–174.4 (7)		

[a] In these averages the bond distances and angles involving the disordered C26 and C34 terminal methyls were not considered. The value in square brackets is the average of the values corrected for riding motion according to Busing and Levy.[9]

bond. The carbonyl ligands are bound to the metal atoms in the coordination planes containing the μ-hydroxo and μ-acetato-*O,O′* oxygens, with the hydroxo group trans to a carbonyl with respect to each metal atom.

The two bulky phosphine ligands approach the metal centers both in directions trans to the μ-acetato-*O* oxygen atom. As usually found with this kind of ligand, the metal–P–C angles [average 114.0 (8)°] are larger than the C–P–C ones [average 104.6 (9)°], as a consequence of some folding of the *n*-butyl groups, in order to reduce steric hindrance. This folding is not the same for the two ligands, as indicated by the effective maximum cone angles,[13,14] which are 150 and 141° for P1 and P2, respectively. These cone angles have been evaluated considering the hydrogen atoms in calculated positions. Also the angles P–C–C [average 115.3 (4)°] are systematically larger than those C–C–C [average 111.8 (9)°] in the chains, owing to the repulsion between the phosphorus atom and the vicinal methylene group [P···CH_2 average 2.840 (16) Å].

The orientation of the alkyl groups with respect to the ligands in the coordination planes opposite to the Ru–P directions is illustrated by the Newman projections of Figure 2, which show that the P–C bonds tend to be intermediate between staggered and eclipsed with respect to the Ru–ligand bonds. These orientations are determined by the C–H···O interactions, quoted in

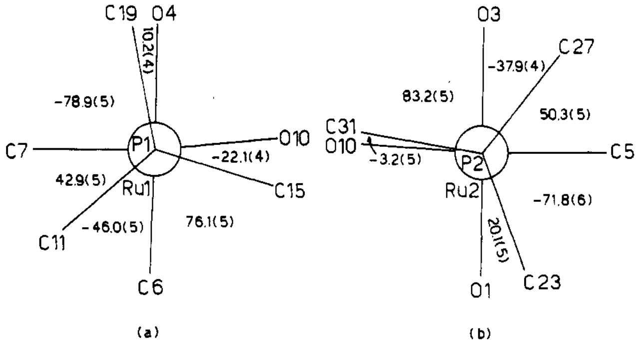

Figure 2. Newman projections: (a) along P1–Ru1; (b) along P2–Ru2 showing the orientation of the phosphine ligands.

Table IV. Intramolecular O–H···O Hydrogen Bonds and the C–H···O Interactions Responsible for the Orientation of the Phosphine Ligands^a

D–H···O	D–H	D···O	H···O	D–H···O
O10–H10···O2	0.74 (6)	2.687 (10)	2.02	152 (5)
C9–H91···O1	1.08	3.468 (13)	2.86	116
C15–H152···O10	1.08	3.142 (11)	2.63	108
C16–H162···O10	1.08	3.484 (13)	2.89	115
C19–H191···O4	1.08	3.056 (13)	2.64	102
C20–H201···O4	1.08	3.212 (15)	2.51	121
C27–H271···O3	1.08	3.163 (13)	2.60	112
C32–H322···O10	1.08	3.295 (16)	2.47	132
C23–H231···O1	1.08	2.910 (15)	2.91	101

[a] Distances are in angstroms and angles are in degrees.

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(13) The "effective" cone angle[14] has been calculated as the double of the angle formed by the Ru–P direction and the tangent from Ru to the most external hydrogen atom sphere to which a van der Waals radius of 1.20 Å has been attributed.

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Table IV; some of them, according to Berkovitch-Yellin and Leiserowitz,[15] can be considered as hydrogen bonds. With reference to this, it is worth noticing that the number of alkyl chains involved in these bonds is equal to the number of the oxygen ligand atoms present in the coordination plane opposite to Ru–P, i.e. two for the P1 and three for the P2 phosphines.

As frequently happens with long alkyl chains, some disorder is observed for the terminal CH_3 groups and this prevented their accurate localization; nevertheless, if exception is made for the disordered C34 methyl group, the C–C bond distances and C–C–C bond angles are quite satisfactory, particularly if the values are corrected for riding motion, as shown by the averages quoted in Table III.

Packing of the complex molecules is due to van der Waals forces.

(c) Spectroscopic Characteristics. In consideration of the fact that different coordination modes cause different shielding of the methyl groups, the resonance at a lower field (δ 2.37) in the ^{1}H NMR spectrum of IV should be associated with the presence of a μ-acetato-*O,O'* ligand containing the most shielded methyl group, that at δ 1.88 with a μ-acetato-*O* ligand, and finally that at δ 1.82 with a terminal acetato.

The engagement of the hydrogen of the μ-OH group in hydrogen bonding toward the O2 oxygen of the terminal acetato group is in keeping with both the low-field resonance (δ 7.34) of the hydrogen (acidic) and the 1678-cm^{-1} band in the IR spectrum. The terminal acetato group, in this situation, behaves very much like a "coordinated acetic acid molecule", giving rise to a decrease of the CO stretching frequency from 1722 cm^{-1}, characteristic of the free acid, to 1678 cm^{-1}. Analogous behavior has been observed in the case of 2-methylbutanoic and benzoic acids present as ligands in ruthenium complexes[16] in which the hydrogens of the acids are engaged in hydrogen bonding with another carboxylate ligand present in the complex.

The absorptions at 1561 and 1592 cm^{-1} may be associated with the μ-CH_3COO-*O,O'* and μ-CH_3COO-*O* groups, respectively.

Experimental Section

IR spectral studies were performed on a Perkin-Elmer 580B data system, and NMR spectra were obtained on a Perkin-Elmer R32 spectrometer. Molecular mass determinations, based on the isopiestic method, were performed on a Wescan Model 233 osmometer. GLC mass spectra were collected by using a Hewlett and Packard apparatus: a Model 5970A chromatograph equipped with a mass detector. The instrument employed for X-ray determinations is reported in Table V.

$Ru(CO)_2(CH_3COO)_2[P(n\text{-}Bu)_3]_2$ (I)[17] and $Ru_4(CO)_8(CH_3COO)_4[P(n\text{-}Bu)_3]_2$ (III)[18] were synthesized according to published methods.

Preparation of $Ru_2(CO)_3(CH_3COO)_3(OH)[P(n\text{-}Bu)_3]_2$ (IV). A solution of I (124.9 mg, 0.189 mmol) and III (120 mg, 0.095 mmol) in 10 mL of *n*-heptane was heated in a sealed glass tube at 120 °C for 150 h. Complexes IV and II, apparently the prevailing products in the crude mixture, were obtained in the ratio 10:1 according to a quantitative IR determination[19] employing the 1991-cm^{-1} absorption for IV and the 2020-cm^{-1} absorption for II.

Slow evaporation of the solvent at room temperature from the crude mixture led to the fractional crystallization of a pale yellow solid IV, yield 20 mg (11.6%).

Anal. Calcd for $C_{33}H_{64}O_{10}P_2Ru_2$: C, 44.79; H, 7.29. Found: C, 44.50; H, 7.20. M_r: calcd, 884.98; found, 860 (*c* 3.57 g/L in toluene).

The presence of CH_3COOH, CH_3COOCH_3, and linear heptenes, in the crude mixture, was proved by comparing GLC mass spectra with those in the literature.[20]

X-ray Crystallographic Study. The relevant data concerning the X-ray analysis are collected in Table V. The space group was assigned on the basis of the systematic absences as found from the list of the processed intensity data. Accurate cell parameters were obtained by using a least-squares procedure with the Nelson and Riley[21] extrapolation function. All data were corrected for Lorentz and polarization effects; corrections for absorption and extinction were applied by using the method of Walker and Stuart.[22]

Table V. Experimental Data for the Crystallographic Analyses of $[P(n\text{-}Bu)_3](CO)_2Ru(\mu\text{-}OH)(\mu\text{-}CH_3COO\text{-}O)(\mu\text{-}CH_3COO\text{-}O,O')Ru(CO)(CH_3COO)[P(n\text{-}Bu)_3]$ (IV)

formula	$C_{33}H_{64}O_{10}P_2Ru_2$
M_r	885.0
habit	small prisms
cryst syst	orthorhombic
space group	*Pbca*
a/Å	32.473 (10)
b/Å	15.342 (5)
c/Å	17.401 (6)
V/Å^3	8669 (5)
Z	8
D_{calcd}/g cm^{-3}	1.356
reflcns for lattice params	
no.	22
θ range/deg	13.4/22.4
radiation for lattice params (λ/Å)	Mo Kα_1 (0.709 300)
F(000)	3680
temp/K	293 (2)
cryst size/mm	0.16 × 0.40 × 0.64
diffractometer	Philips PW1100
μ/mm^{-1}	0.80
abs cor (min–max)	0.996–1.082
extincn cor (min–max)	0.947–1.005
scan speed/deg s^{-1}	0.075
scan width/deg	1.40
radiation for intens meas (λ/Å)	Mo K$\bar{\alpha}$ (0.710 69)
θ range/deg	3–26
h range	0–40
k range	0–19
l range	0–22
std reflcn	11,4,3
intens var	<2%
scan mode	$\omega/2\theta$
no. of measd reflcns	9302
condition for obs reflcns	$I \geq 2\sigma(I)$
no. of reflcns used in the refinement	4193
anisotropic least squares on F	block diagonal
mean least-squares shift to error ratio	0.108
min–max height in final $\Delta\rho$/e Å^{-3}	–0.14 to 0.12
no. of refined params	546
R^a	0.0697
$R_w{}^b$	0.0629
S^c	1.9561

$^aR = \sum|\Delta F|/\sum|F_o|$. $^bR_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$. $^cS = [\sum w(\Delta F)^2/(N - P)]^{1/2}$.

The structure was solved by Patterson and Fourier methods using the SHELX84[23] program and refined by the SHELX76 program.[24] The atomic scattering factors and anomalous scattering coefficients are from ref 25.

The calculations were carried out on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy. In addition to the previously quoted programs, the PARST,[26] LQPARM,[27] ORTEP,[28] and ABSORB[29] programs have also been used.

Throughout the paper the averaged values are weighted means with weights equal to the reciprocal of the squared esd's. When two values are compared, the statistical significance of the difference is evaluated

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by the ratio Δ/σ of the difference from its esd.

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Supplementary Material Available: Figure A (IR spectra of $Ru(CO)_2(CH_3COO)_2[P(\textit{n}-Bu)_3]_2$ and $Ru_4(CO)_8(CH_3COO)_4[P(\textit{n}-Bu)_3]_2$ in heptane at 60, 100, 120, and 140 °C) and, for IV, Figure B (IR spectrum, KBr pellet) and Figure C (NMR spectrum, CD_2Cl_2 solution) and, for the structure determination, tables of anisotropic thermal parameters, hydrogen atom coordinates, bond distances, bond angles, and torsion angles (17 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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Two New Nickel Difluorophosphine Species: Synthesis, Characterization, and Discussion Regarding the Nature of the Nickel–Difluorophosphine Interaction

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The study of the coordination chemistry of PF_2H has been expanded by the synthesis and characterization of $Ni(CO)_3(PF_2H)$ and $Ni(CO)_2(PF_2H)_2$. Spectral data for these complexes are compared with those of related compounds as a probe for investigating bonding interactions of PF_2H. Infrared carbonyl stretching frequency data and displacement reactions suggest that the electron-donor–electron-acceptor properties of PF_2H are intermediate between those of PF_3 and PH_3 when the ligands are bound to nickel. This observation contrasts sharply with the donor ability of PF_2H when BH_3 is the reference acid. In the latter case PF_2H is a much stronger base than PF_3 or PH_3. Acid–base arguments are considered.

The chemistry of PF_2H has been a widely discussed topic in the literature for several years.[1] $HF_2P{\cdot}BH_3$,[2] and $HF_2P{\cdot}B_4H_8$[3,4] show an unexpectedly high thermal stability when compared with the analogous complexes of PF_3 and PH_3. This anomalous behavior of PF_2H has been interpreted as evidence for the premise that PF_2H is a stronger σ base than either PF_3 or PH_3.[5] In contrast, $Ni(PF_2H)_4$ is intermediate in thermal stability between $Ni(PF_3)_4$ and $Ni(PH_3)_4$.[6]

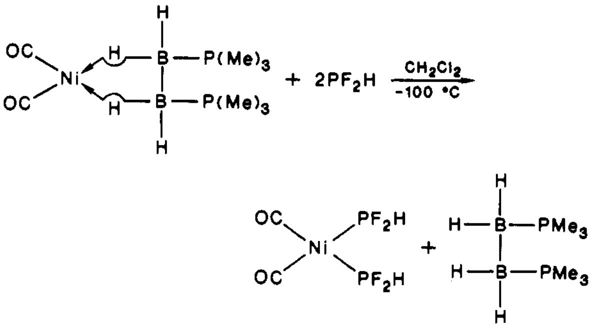
We were interested in synthesizing $Ni(CO)_3(PF_2H)$ and $Ni(CO)_2(PF_2H)_2$ to obtain more definitive information concerning the electron-donor–electron-acceptor properties of PF_2H. Carbonyl infrared stretching frequencies are generally free from extensive coupling with other modes and they usually are not obscured by the presence of other vibrations, so they provide a useful probe into bonding considerations. Tolman[7] and others[8] have previously used carbonyl infrared data as one measure of the relative electron-donor–electron-acceptor properties of phosphorus ligands bound to metal carbonyls. In this paper we have compared the infrared data for $Ni(CO)_3L$ and $Ni(CO)_2L_2$ where L = PF_3, PF_2H, and PH_3 in order to compare PF_2H to other related ligands. These results will be discussed. Some displacement results are also considered.

Prior to this study, $Ni(PF_2H)_4$ was the only well-characterized, isolatable metal complex of PF_2H.[6,9] So far PF_2H complexes are more difficult to prepare than most other analogous phosphine metal complexes,[6,10,11] because of the high reactivity of PF_2H itself. The compound is air and water sensitive and will begin to decompose or react readily when it is in an impure state, even at temperatures of 20 °C or lower. However, when PF_2H is pure, it can be held at room temperature for short periods of time with minimal decomposition and it can be handled very easily by using high-vacuum techniques.[12] $(CO)_3Ni(PF_2H)$ is easily prepared by using general procedures described earlier[13] for the preparation of $Ni(CO)_3L$ species where L is a phosphine. The equation is

$$PF_2H + Ni(CO)_4\ (excess) \xrightarrow[-80\ °C]{CH_2Cl_2} (CO)_3Ni(PF_2H) + CO \qquad (1)$$

$Ni(CO)_2(PF_2H)_2$ is also easily prepared by exploiting the reactive

bonds in the complex $Ni(CO)_2(B_2H_4{\cdot}2PMe_3)$.



(2)

This method has also been used to prepare $Ni(CO)_2L_2$ complexes where L = PPh_3, PF_3, and PH_3.[14]

Experimental Section

General Methods. All manipulations were carried out under an inert atmosphere or on a high-vacuum line. IR data were recorded on a Beckman IR-20 high-resolution spectrometer or on a Perkin-Elmer 1500 FTIR spectrometer. Mass spectral data were obtained by using a VG

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