Articles

Synthesis, Characterization, and Reactivity of the Carboxylate Dimers $[Rh(\mu\text{-}OOCCR_3)(CO)(PCy_3)]_2$ (R = H, F). X-ray Crystal Structure of $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(CO)_2(PCy_3)_2]$

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The synthesis of dinuclear complexes of formulas $[Rh(\mu\text{-}OOCCR_3)(CO)(PCy_3)]_2$ (R = H (7), F (8)) and $[Rh_2(\mu\text{-}OOCCR_3)_2(CO)_3(PCy_3)]$ (R = H (11), F (12)) is described. These dinuclear compounds react with dimethyl acetylenedicarboxylate to form $[Rh_2(\mu\text{-}OOCCR_3)_2(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_2(PCy_3)_2]$ (R = H (13), F (14)) and $[Rh_2(\mu\text{-}OOCCR_3)_2(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_3(PCy_3)]$ (R = H (16), F (17)), respectively. The subsequent treatment of 13 with this alkyne gives $[Rh_2(\mu\text{-}OOCCH_3)_2(\mu\text{-}MeO_2CC{=}CCO_2Me)(\eta^2\text{-}MeO_2CC{=}CCO_2Me)(CO)_2(PCy_3)]$ (15). The addition of terminal alkynes to acetone solutions of 7 leads to the formation of compounds of the type $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2R)(CO)_2(PCy_3)_2]$ (R = Ph (18), Cy (19), Me_3Si (20), MeO_2C (21)). Similarly $[Rh_2(\mu\text{-}OOCCF_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(CO)_2(PCy_3)_2]$ (22) and $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(COD)_2]$ (23) are prepared by the reaction of PhC≡CH with 8 and $[Rh(\mu\text{-}OOCCH_3)(COD)]_2$ (1), respectively. The molecular structure of 18 was determined by X-ray investigations. 18 crystallizes in the space group $P2_1/n$ with a = 16.418 (7) Å, b = 15.715 (3) Å, c = 20.117 (8) Å, and β = 112.92 (2)°. The complex can be described as a coordinatively unsaturated dinuclear compound, where the coordination geometry around each rhodium atom is approximately square-planar. The phenylacetylide ligand acts as a three-electron donor ligand which is bound σ to one rhodium atom and π to the other. In solution there is a rapid σ/π transformation of the alkynyl group between the metal atoms. ETH calculations on the fluxional movement in the model compound $[Rh_2(\mu\text{-}OOCH)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2H)(CO)_2(PH_3)_2]$ suggest that the process has a low activation barrier (ca. 0.5 eV at the ETH level). The synthesis of the complexes $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}pz)(CO)_2(PCy_3)_2]$ (24), $[Rh(\mu\text{-}pz)(CO)(PCy_3)]_2$ (25), and $[Rh(OCOCF_3)(CO)(Hpz)(PCy_3)]$ (26) is also described.

Introduction

We have recently reported that 1-(4-pyridylmethylene)-4-alkoxyanilines ($L^n = NC_5H_4CH{=}NC_6H_4OC_nH_{2n+1}$) split the bridge of the complexes $[M(\mu\text{-}Cl)(COD)]_2$ (M = Rh, Ir) to give mononuclear species of the type $[MCl(COD)L^n]$, which afford *cis*-dicarbonyl compounds, $[MCl(CO)_2L^n]$ (M = Rh, Ir), by reaction with CO. These dicarbonyl complexes are stable in solution. In the solid state, at temperatures higher than 60 °C, they show mesogenic properties.[1,2] In a continuation of our work in this field, we subsequently reported the synthesis of the carboxylate compounds $[Rh(OCOCR_3)(CO)_2L^n]$ (R = H, F), which were obtained by reaction of ligands L^n with the corresponding dimers $[Rh(\mu\text{-}OOCCR_3)(CO)_2]_2$ (R = H, F). In the solid state, these complexes do not show mesogenic properties. In solution, they decomposed into the square-planar clusters $[Rh_4(\mu\text{-}OOCCR_3)_4(\mu\text{-}CO)_4L^n_4]$. The molecular structure of these clusters, determined by X-ray diffraction, can be described as two crystallographically independent dinuclear "$Rh_2(OCOCR_3)_2(\mu\text{-}CO)_2L^n_2$" moieties held together by two Rh–Rh metal bonds and four bridging carboxylate ligands, giving rise to a tetranuclear cluster with the metal atoms defining a slightly distorted square plane.[3]

The reaction of the dimers $[Rh(\mu\text{-}OOCCR_3)(CO)_2]_2$ (R = H, F) with pyridine (py) leads also to the formation of the related clusters $[Rh_4(\mu\text{-}OOCCR_3)_4(\mu\text{-}CO)_4(py)_4]$, via the mononuclear intermediates $[Rh(OCOCR_3)(CO)_2(py)]$ (R = H, F). However, by reaction of $[Rh(\mu\text{-}OOCCR_3)(CO)_2]_2$ with PCy_3, the dimers $[Rh(\mu\text{-}OOCCR_3)(CO)(PCy_3)]_2$ are obtained.

In this paper, we report the synthesis and characterization of the complexes $[Rh(\mu\text{-}OOCCR_3)(CO)(PCy_3)]_2$ (R = H, F) and their reactivity toward $MeO_2CC{=}CCO_2Me$, PhC≡CH, CyC≡CH, $Me_3SiC{\equiv}CH$, $MeO_2C{\equiv}CH$, and pzH (pyrazole). In addition, the X-ray crystal structure

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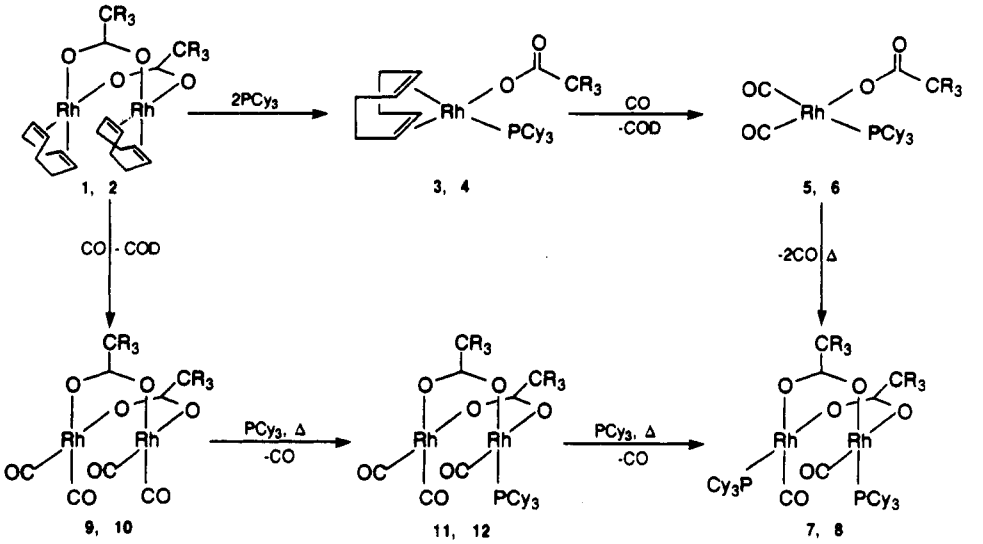
Scheme I



R= H (1, 3, 5, 7, 9, 11), F (2, 4, 6, 8, 10, 12)

COD (1,5-cyclooctadiene)

Table I. IR and $^{31}P\{^1H\}$ NMR Data for the Complexes 3–8 and 11–26

	IR (cm^{-1})[a]				$^{31}P\{^1H\}$ (PCy_3)	
	M–CO	R_3COO				
complex	ν(CO)	ν_{asym}(OCO)	ν_{sym}(OCO)	$\Delta\nu$	δ (ppm)	J_{Rh-P} (Hz)
3		1640	1375	265	26.2[b]	148
4		1693			27.3[c]	145
5	2075, 1988	1625	1380	245	41.6[c]	131
6	2085, 2052	1689			41.7[c]	127
7	1960	1600	1440	160	60.3[b]	175
8	1980	1682			62.3[c]	174
11	2071, 2005, 1951	1579	1426	153	61.6[c]	169
12	2090, 2029, 1979	1660			64.3[c]	168
13[d]	2025, 1993	1575	1440	135	19.5 (AA′XX′)[b,e]	55, 43
14[d]	2046, 2011	1585			22.9 (AA′XX′)[c,e]	57, 43
15[d]	2050, 2001	1575	1440	135	17.4 (AMX)[b]	97, 35
16[d]	2040, 1990	1555	1405	150	16.3 (AMX)[b]	97, 34
17[d]	2059, 2027	1572			38.4 (AMX)[c]	98, 24
18	1975, 1950	1575	1450	125	45.9[b]	151
19	1974, 1952	1565	1450	115	45.3[c]	149
20	1970, 1940	1565	1450	115	40.0[c]	146
21	1970, 1952	1549	1445	104	45.1[c]	149
22	1985, 1960	1686			45.7[c]	145
23		1560	1425	135		
24	1969, 1955	1600	1440	160	59.0[b]	177
					53.2	145
25	1965				51.7[b]	147
26	1975	1675			55.4[c]	152

[a] In Nujol. [b] In $CDCl_3$. [c] In C_6D_6. [d] ν(CO) = 1712 cm^{-1} ($MeO_2CC{=}CCO_2Me$). [e] $J_{AA'}$ = 0.

of the complex $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(CO)_2(PCy_3)_2]$ is described.

Results and Discussion

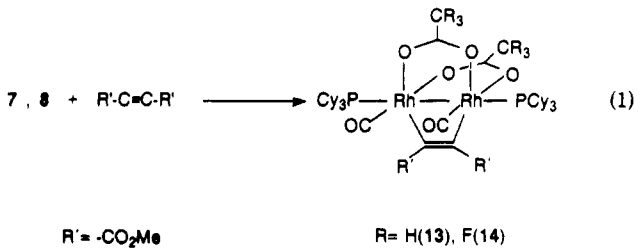
1. Synthesis and Characterization of $[Rh(\mu\text{-}OOCCR_3)(CO)(PCy_3)]_2$ (R = H, F). The two routes employed for the preparation of the dinuclear compounds $[Rh(\mu\text{-}OOCCR_3)(CO)(PCy_3)]_2$ (R = H, F) are summarized in Scheme I. Treatment of $[Rh(\mu\text{-}OOCCR_3)(COD)]_2$ (R = H (1), F (2)) with PCy_3 in a 1:2 molar ratio, in hexane, leads to the square-planar complexes $[Rh(OCOCR_3)(COD)(PCy_3)]$ (R = H (3), F (4)). Bubbling CO through a hexane suspension of 3 or 4 results in the displacement of the coordinated diolefin and formation of *cis*-$[Rh(OCOCR_3)(CO)_2(PCy_3)]$ (R = H (5), F (6)). Under reflux in hexane, 5 and 6 decompose into 7 and 8. Alternatively, 7 and 8 can be prepared by starting from 9 and 10. Compounds 9 and 10 react with PCy_3 in a 1:1 molar ratio in hexane to give the dinuclear complexes 11 and 12, which in the presence of PCy_3, under reflux in hexane, are converted into 7 and 8.

The IR and ^1H and $^{31}P\{^1H\}$ NMR spectra of the complexes 3–8, 11, and 12 (see Table I and Experimental Section) are in good agreement with the structures proposed in Scheme I. In the IR spectra of 5 and 6 in Nujol there are two strong ν(CO) bands around 2000 cm^{-1} consistent with the cis geometry. The terminal carbonyl ligands of 11 and 12 give rise to three ν(CO) bands in the same spectral region, while 7 and 8 give rise to only one

band, which is also consistent with the proposed structures. The carboxylate ligands are formulated as monodentate ligands in **3–6** and as bidentate ligands in **7**, **8**, **11**, and **12** on the basis of the values found for $\Delta\nu$ ($\nu_{asym}(OCO) - \nu_{sym}(OCO)$), which coincide with those previously found for related compounds containing 1-(4-pyridylmethylene)-4-alkoxyanilines[3] and with those reported by Mitchell et al.,[4] Robinson et al.,[5] and Deacon et al.[6] for the same ligands in other types of compounds. The ^1H NMR spectra of **3** and **4** contain two peaks due to two groups of two chemically inequivalent 1,5-cyclooctadiene vinyl protons, suggesting that these complexes have a rigid square-planar structure in solution. This is in contrast to the case for the complexes $[RhCl(COD)L^n]$, $[Rh(OCOCR_3)(COD)L^n]$, and related rhodium and iridium compounds of formula [MX(COD)L], where the existence of a rapid exchange process has been suggested, in order to explain the equivalence of the vinylic 1,5-cyclooctadiene protons.[7] $^{31}P\{^1H\}$ NMR spectra of the complexes shown in Scheme I contain a doublet between 27 and 68 ppm with a Rh–P coupling constant of about 130–140 Hz for the mononuclear compounds **3–6** and about 165–175 Hz for the dinuclear compounds **7**, **8**, **11**, and **12**. The multiplicity of the signals of **7**, **8**, **11**, and **12** suggests that these compounds do not contain metal–metal bonds, in contrast to the complex $[Rh_2(\mu\text{-}OOCCH_3)_2(CO)_3(PPh_3)]$, where a rhodium–rhodium bond has been proposed.[8] The dinuclear character of these compounds was confirmed by osmometrical determination, in $CHCl_3$, of the molecular weight of **7**. The value obtained, 969, agrees well with that calculated for the formula $[Rh(\mu\text{-}OOCCH_3)(CO)(PCy_3)]_2$ (941.0).

In order to understand why square-planar clusters of formula $[Rh_4(\mu\text{-}OOCCR_3)_4(\mu\text{-}CO)_4L^n_4]$ cannot be obtained when L is the tricyclohexylphosphine ligand, an EHT-MO calculation was carried out on the generic phosphine complex $[Rh_4(\mu\text{-}OOCH)_4(\mu\text{-}CO)_4(PH_3)_4]$. A simple fragment analysis of the interaction of $Rh_4(\mu\text{-}OOCH)_4(\mu\text{-}CO)_4$ with four phosphine groups shows that there is sizable repulsive interaction between the phosphine ligands, which might be attributed to steric interactions. This fact seems to prevent the isolation of tetranuclear species analogous to $[Rh_4(\mu\text{-}OOCCR_3)_4(\mu\text{-}CO)_4(py)_4]$ (R = H, F), with four tricyclohexylphosphine groups.

2. Reactions of 7 and 8. Complexes **7** and **8** react with the electron-withdrawing alkyne dimethyl acetylenedicarboxylate in a 1:1 molar ratio to form yellow compounds analyzed as $[Rh_2(OOCCR_3)_2(MeO_2CCCCO_2Me)(CO)_2(PCy_3)_2]$ (R = H (**13**), F (**14**)). Two bonding modes have been described for the dimethyl acetylenedicarboxylate ligand: the pseudotetrahedral μ-η^2 mode, in which the alkyne is disposed perpendicularly to the metal–metal axis, and the cis-dimetalated olefinic mode, in which the carbon–carbon double bond is parallel to the metal–metal axis.[9] With regard to the spectroscopic data, there is no doubt that in **13** and **14** the acetylene is symmetrically bound as a dimetalated olefin (eq 1). Thus, the reactions of **7** and

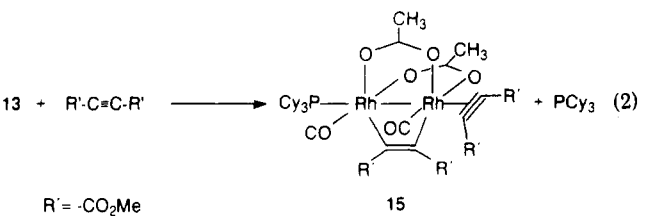


(1)

8 with $C_2(CO_2Me)_2$ involve a one-electron oxidative addition to each rhodium center with formation of a rhodium–rhodium bond and, consequently, the $^{31}P\{^1H\}$ NMR spectra of these compounds show second-order AA′XX′ splitting patterns. In addition, only one peak due to two magnetically equivalent $-CO_2CH_3$ groups is observed in the ^1H NMR spectra. The IR spectra (Table I) are also in good agreement with the proposed structure, as shown in eq 1.

It should be mentioned that the X-ray crystal structure of the analogous compound $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_2\{P(OMe)_3\}_2]$ has been recently reported. This complex was prepared similarly to **13** and **14**, by addition of the acetylene to a dichloromethane solution of the dimer $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(CO)_2\{P(OMe)_3\}_2]$.[10] Related complexes of rhodium[11] and iridium[12] had been previously described.

In hexane under reflux, **13** reacts with dimethyl acetylenedicarboxylate to give **15** and PCy_3 (eq 2).



(2)

Compound **15** was fully characterized by elemental analysis and IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. In agreement with the proposed structure, the $^{31}P\{^1H\}$ NMR spectrum in chloroform shows a four-line pattern centered at δ 17.4 of relative intensities 1:1:1:1 (AMX system, J_{Rh-P} = 97 and $J_{Rh'-P}$ = 35 Hz). In addition four peaks due to four chemically inequivalent $-CO_2CH_3$ groups at 3.88, 3.78, 3.77, and 3.66 ppm are observed in the ^1H NMR spectrum.

The compounds **11** and **12** also react with dimethyl acetylenedicarboxylate. Thus, the complexes $[Rh_2(\mu\text{-}OOCCR_3)_2(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_3(PCy_3)]$ (R = H (**16**), F (**17**)) were obtained similarly to **13** and **14**, by

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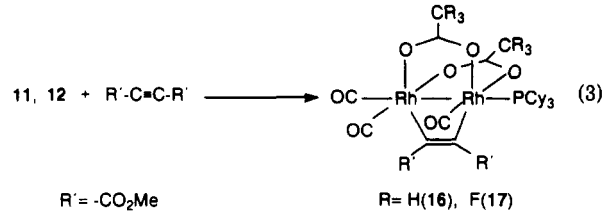
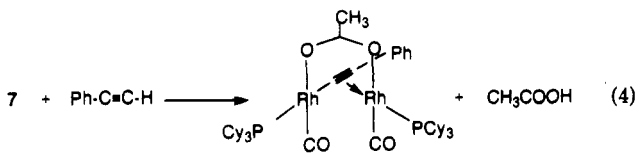
(12) (a) El Amane, M.; Mathieu, R.; Poilblanc, R. *Organometallics* **1983**, *2*, 1618. (b) Guilmet, E.; Maisonnat, A.; Poilblanc, R. *Organometallics* **1983**, *3*, 1123. (c) Sutherland, B. R.; Cowie, M. *Organometallics* **1984**, *3*, 1869. (d) Mague, J. T.; Klein, C. L.; Majeste, R. J. Stevens, E. D. *Organometallics* **1984**, *3*, 1860. (e) Cowie, M.; Vasapollo, G.; Sutherland, B. R.; Ennet, J. P. *Inorg. Chem.* **1986**, *25*, 2653.

addition of the alkyne to hexane suspensions of **11** and **12** in a 1:1 molar ratio (eq 3).



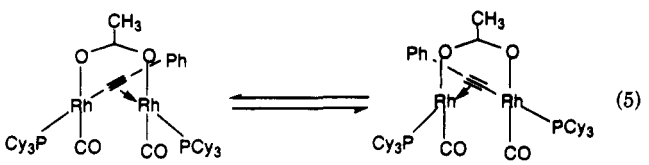
In keeping with the proposed structures, the $^{31}P\{^1H\}$ NMR spectra of these compounds exhibit AMX splitting patterns with Rh–P coupling constants of about 97 Hz and Rh′–P coupling constants between 25 and 35 Hz. In addition, the ^1H NMR spectra contain two signals assigned to the protons of the methyl group of the dimetalated olefin. Similarly to **13–15**, the IR spectra of **16** and **17** have two ν(CO) bands in the M–CO region (Table I). The presence of three terminal carbonyl ligands in these molecules was deduced from the $^{13}C\{^1H\}$ NMR spectrum of **17**, which contains three complex signals at 194.7, 188.3, and 186.3 ppm.

The reaction of **7** with phenylacetylene was found not to lead to a cis-dimetalated olefinic complex. The addition of the alkyne to **7** in acetone solution led to the isolation of the complex $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2Ph)(CO)_2(PCy_3)_2]$ (**18**) as an orange solid in 61% yield, according to eq 4.



18

A single-crystal X-ray diffraction analysis of **18** demonstrates the $\mu\text{-}\eta^1\text{:}\eta^2$ binding mode of the alkynyl ligand (see below). Of particular note is the fact that the $^{31}P\{^1H\}$ NMR spectrum exhibits a doublet at δ 45.9 with a Rh–P coupling constant of 151 Hz, establishing that there is a rapid oscillation of the alkynyl group between the two metal atoms, in solution (eq 5). Such a process has also

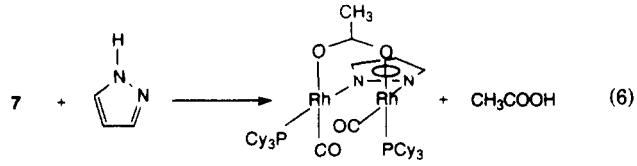


been observed for the cyanide ligand in the complexes $[Rh_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CN)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$,[13] $(NEt_4)[Cp_2Mo_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CN)(CO)_3]$,[14] and $[Mn_2H(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CN)(CO)_4(\mu\text{-}dppm)_2]$[15] and for the alkynyl group in the complexes $[Rh_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2R)(CO)_2(\mu\text{-}dppm)_2]ClO_4$[16] (R = *t*-Bu, Ph, H). As found for these compounds, the motion of the alkynyl group in **18** is still rapid at –60 °C.

The compounds $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2R)(CO)_2(PCy_3)_2]$ (R = Cy (**19**), Me_3Si (**20**), MeO_2C (**21**)), obtained similarly to **18**, show the same dynamic behavior in solution. In the presence of terminal alkynes the trifluoroacetate compound **8** is more stable than **7**. Thus, **8** does not react with cyclohexylacetylene, (trimethylsilyl)acetylene, and methyl propiolate, while the reaction with phenylacetylene gives an orange solid formed from $[Rh_2(\mu\text{-}OOCCF_3)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2Ph)(CO)_2(PCy_3)_2]$ (**22**) and **8** in a ca. 1:1 molar ratio. The diolefin complex **1** also reacts with phenylacetylene. Working under conditions similar to those mentioned for **18**, we have isolated red-orange crystals of formula $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2Ph)(COD)_2]$ (**23**). The ^1H and $^{13}C\{^1H\}$ NMR spectra of this complex (see Experimental Section) suggest that the alkynyl ligand is also oscillating between the two metal centers.

The dynamic oscillation process of the alkynyl group between the two rhodium atoms of **18–23** involves, most probably, a symmetrical $Rh_2(\mu\text{-}\eta^1\text{-}C_2R)$ bonding mode. An EHT-MO calculation on the fluxional movement in the model compound $[Rh_2(\mu\text{-}OOCH)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2H)(CO)_2(PH_3)_2]$ shows that the process has a low activation barrier (ca. 0.5 eV at the EHT level). As shown in the Walsh diagram in Figure 1, there is not any significant energy change in the molecular orbitals during the process. In a symmetrically bridging arrangement, $[Rh_2(\mu\text{-}OOCH)(\mu\text{-}\eta^2\text{-}C_2H)(CO)_2(PH_3)_2]$, the lone pair on the alkynyl ligand 5a′ overlaps with the occupied fragment orbitals 15a′ and 18a′ and with the empty fragment orbital 19a′ of the $[Rh_2(\mu\text{-}OOCH)(CO)_2(PH_3)_2]$ moiety (Figures 2 and 3). This overlap generates a typical three-center–four-electron pattern which gives a net bonding character to the interaction between the rhodium atoms and the alkynyl ligand. On the other hand, one of the π orbitals (4a′) of the alkynyl ligand remains nonbonding, whereas the other (3a′) overlaps with the dirhodium fragment in such a fashion that both the bonding and the antibonding combinations are occupied. In the asymmetrically bonded species $[Rh_2(\mu\text{-}OOCH)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2H)(CO)_2(PH_3)_2]$ the lone pair and the π electrons of the alkynyl ligand take part in a large number of molecular orbitals of the final complex (Figure 4). In Chart I are reflected the changes in the carbon–rhodium overlap populations for the two bonding modes of the alkynyl group. The reduced overlap population between the dirhodium fragment and the alkynyl group summarizes the overall result of the interaction. When the alkynyl ligand is bound to the metal atoms in a symmetric bridging mode, the interaction is weaker (0.63) than when the alkynyl ligand is disposed in the asymmetric fashion (0.81).

There is also a marked difference in reactivity between **7** and **8** toward pyrazole. Whereas the acetate complex **7** reacts with pyrazole, in acetone at room temperature in a 1:1 molar ratio, to give the yellow dimer $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}pz)(CO)_2(PCy_3)_2]$ (**24**) (eq 6), the trifluoroacetate complex **8** is completely inert under such conditions.



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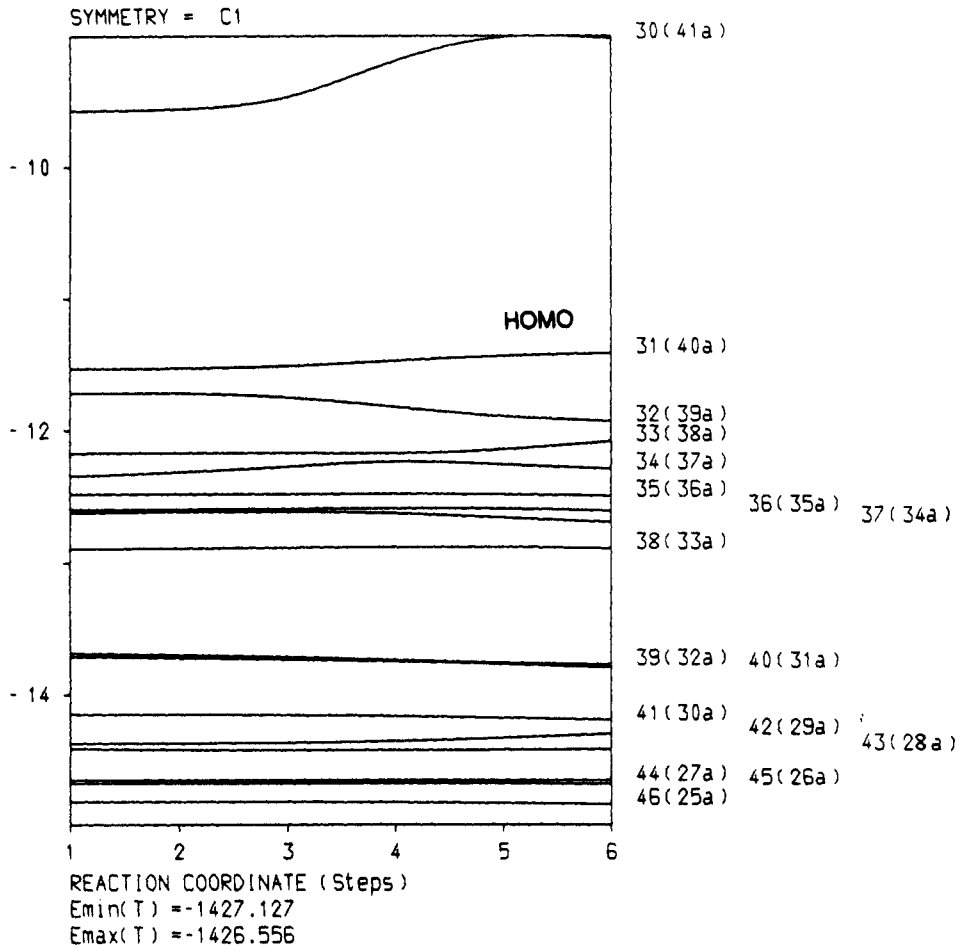


Figure 1. Walsh diagram for the interconversion process from $[Rh_2(\mu\text{-}OOCH)(\mu\text{-}\eta^1\text{-}C_2H)(CO)_2(PH_3)_2]$ to $[Rh_2(\mu\text{-}OOCH)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2H)(CO)_2(PH_3)_2]$.

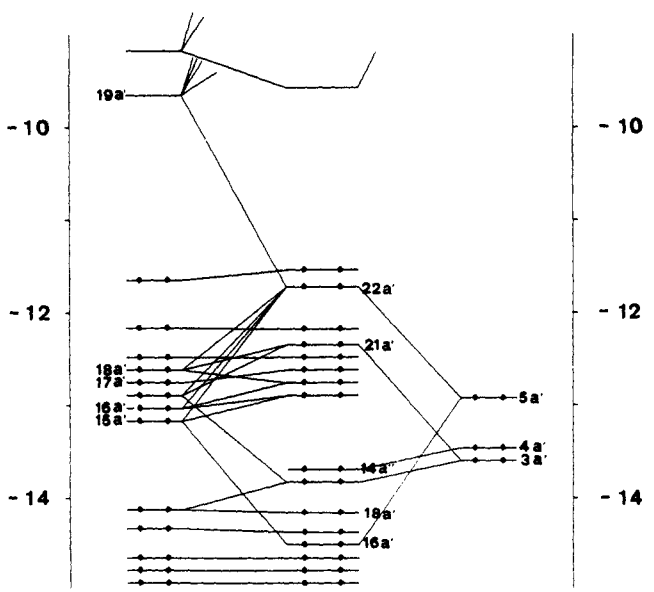


Figure 2. Fragment molecular orbital interaction diagram between $(C_2H)^-$ and $[Rh_2(\mu\text{-}OOCH)(PH_3)_2(CO)_2]^+$ to give the complex $[Rh_2(\mu\text{-}OOCH)(\mu\text{-}\eta^1\text{-}C_2H)(CO)_2(PH_3)_2]$. The lines linking the orbital energy levels represent participations larger than 12%.

In agreement with the proposed structure for **24**, the $^{31}P\{^1H\}$ NMR spectrum of this complex shows two doublets at δ 59.0 and 53.2 with Rh–P coupling constants of 171 and 145 Hz, respectively. On the other hand, this splitting pattern suggests that **24** does not contain a rhodium–rhodium bond, in contrast to **13** and **14** where, due to the metal–metal bond of these compounds, second-order splitting patterns AA'XX' are observed. The complex **24** reacts also with pyrazole in acetone at room temperature in a 1:1 molar ratio, to give $[Rh(\mu\text{-}pz)(CO)(PCy_3)]_2$ (**25**) and acetic acid. Compound **25** can be alternatively obtained by direct reaction of **7** and pyrazole in a 1:2 molar ratio. Under the same conditions, **8** reacts with pyrazole to give the complex $[Rh(OCOCF_3)(CO)(Hpz)(PCy_3)]$ (**26**).

3. Molecular Structure of $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2Ph)(CO)_2(PCy_3)_2]$ (18). A partial view of the molecular geometry of this compound is shown in Figure 5. Selected bond distances and angles are listed in Table II.

The complex can be described as a coordinatively unsaturated dinuclear compound, where the coordination geometry around each rhodium atom is approximately square-planar. The rhodium–rhodium distance is 3.1790 (6) Å, indicating that **18** does not contain a metal–metal bond. The phenylacetylide ligand acts as a three-electron-donor ligand bound to the Rh(1) atom in a slightly bent way, as is shown by the Rh(1)–C(1)–C(2) angle of 173.9°. The Rh(1)–C(1) bond length (2.009 (5) Å) is consistent with a single bond from Rh(1) to a C(sp) atom. The π interaction between the C(1)–C(2) triple bond (1.238 (7) Å) and the Rh(2) atom is rather asymmetrical; the Rh(2)–C(1) and the Rh(2)–C(2) bond lengths are 2.283 (5) and 2.385 (5) Å, respectively. A similar disposition of the triple bond of the alkynyl group has been previously found in the complexes $[Mn_2(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2Ph)(CO)_6(\mu\text{-dp-}$

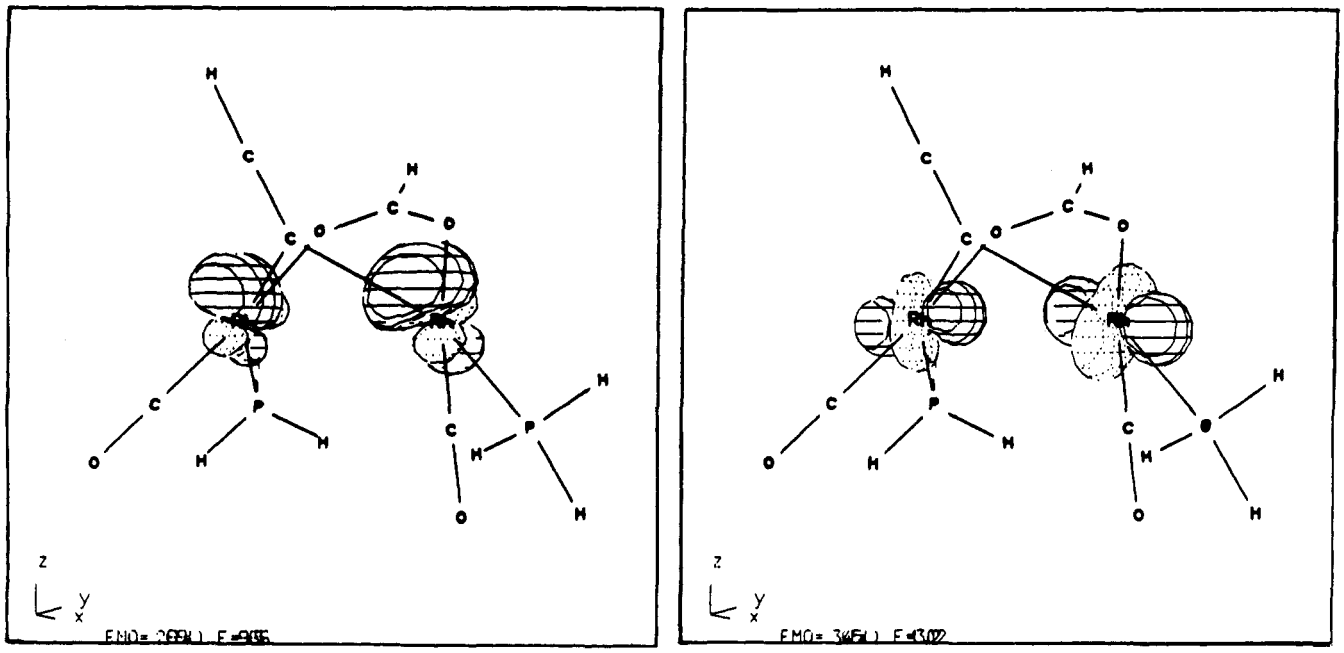


Figure 3. Fragment molecular orbitals 19a′ (left) and 15a′ (right) corresponding to the cation $[Rh_2(\mu\text{-}OOCH)(PH_3)_2(CO)_2]^+$.

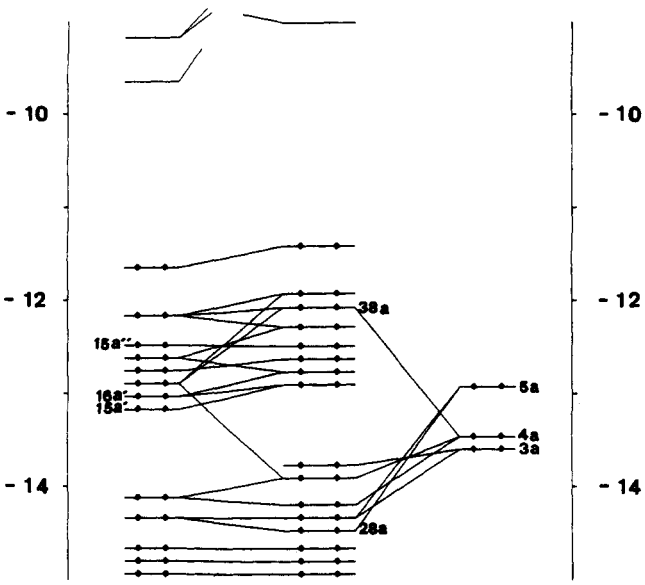
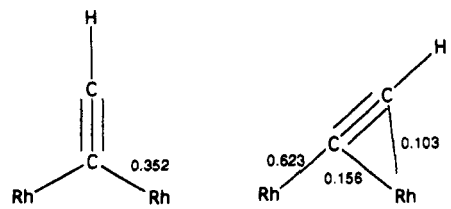


Figure 4. Fragment molecular orbital interaction diagram between $(C_2H)^-$ and $[Rh_2(\mu\text{-}OOCH)(PH_3)_2(CO)_2]^+$ to give the complex $[Rh_2(\mu\text{-}OOCH)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2H)(CO)_2(PH_3)_2]$. The lines linking the orbital energy levels represent participations larger than 12%.

Chart I



pm)],[17] $[ClPt(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Me)(\mu\text{-dppm})_2Rh(CO)]PF_6$,[18] and $[Rh_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2\text{-}t\text{-Bu})(dppm)]$.[19]

For both rhodium atoms, the alkynyl–rhodium bonds are disposed trans to the tricyclohexylphosphine ligands (P(1)–Rh(1)–C(1) = 177.0 (1)° and P(2)–Rh(2)–C(1) = 171.7 (1)°). Thus, the different structural influences of the bonds Rh–(η^1-C_2Ph) and Rh–(η^2-C_2Ph) are seen in the significant differences in the Rh–P distances. The Rh(1)–P(1) distance is 2.341 (1) Å, while the Rh(2)–P(2) distance is 2.285 (1) Å.

The other two corners around each rhodium atom are occupied by the CO ligands and the oxygen atoms of the acetate group, disposed mutually trans. The corresponding bond distances and angles are in the expected range and deserve no further comment.

4. Concluding Remarks. The results reported by us, in this and previous[3] papers, show that the products obtained by the reaction of $[Rh(\mu\text{-}OOCCR_3)(CO)_2]_2$ (R = H (**9**), F (**10**)) with nitrogen and phosphorus donor ligands depend on the nature of the donor atom of the ligands. Thus, the reactions with 1-(4-pyridylmethylene)-4-alkoxyanilines and pyridine lead to the square-planar cluster $[Rh_4(\mu\text{-}OOCCR_3)_4(\mu\text{-}CO)_4L^n{}_4]$ via the mononuclear intermediates $[Rh(OCOCR_3)(CO)_2L]$, while in the presence of tricyclohexylphosphine the dimers $[Rh(\mu\text{-}OOCCR_3)(CO)(PCy_3)]_2$ (R = H (**7**), F (**8**)) are obtained. EHT-MO calculations studies suggest that steric interactions between the phosphine ligands prevent the isolation of square-planar clusters, analogous to those obtained with pyridine and 1-(4-pyridylmethylene)-4-alkoxyaniline.

Compounds **7** and **8** have a marked reactivity toward alkynes. They, as well as **11** and **12**, react with dimethyl acetylenedicarboxylate to give $[Rh_2(\mu\text{-}OOCCR_3)_2(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_2(PCy_3)_2]$ (R = H (**13**), F (**14**)) and $[Rh_2(\mu\text{-}OOCCR_3)_2(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_3(PCy_3)]$ (R = H (**16**), F (**17**)), respectively. These reactions involve a one-electron oxidative addition to each rhodium atom of the dinuclear starting materials with formation of a rhodium–rhodium bond in the resulting products. Although **7** shows the same reactivity as **8** toward dimethyl acetylenedicarboxylate, there is a pronounced difference between these compounds in reactivity toward terminal

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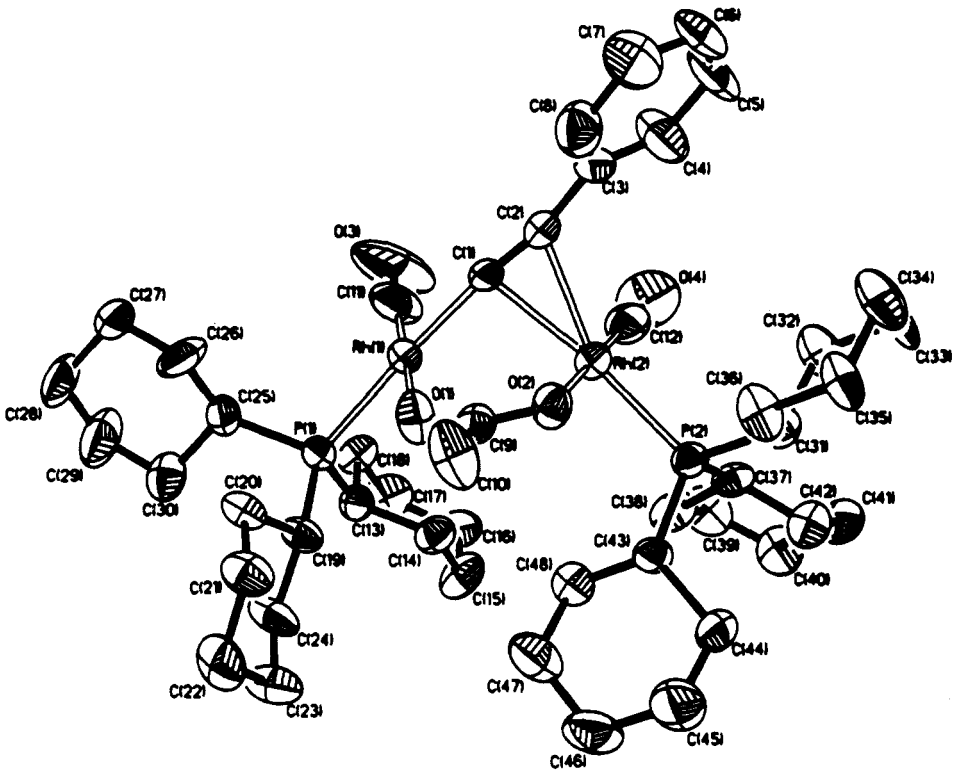

Figure 5. ORTEP diagram of $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(CO)_2(PCy_3)_2]$ (**18**). Thermal ellipsoids are shown at the 50% level.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations

Bond Distances			
Rh(1)–P(1)	2.341 (1)	Rh(2)–C(12)	1.805 (8)
Rh(1)–O(1)	2.088 (4)	O(1)–C(9)	1.261 (6)
Rh(1)–C(1)	2.009 (5)	O(2)–C(9)	1.258 (6)
Rh(1)–C(11)	1.771 (8)	O(3)–C(11)	1.154 (9)
Rh(2)–P(2)	2.285 (1)	O(4)–C(12)	1.130 (8)
Rh(2)–O(2)	2.083 (4)	C(1)–C(2)	1.238 (7)
Rh(2)–C(1)	1.283 (5)	C(2)–C(3)	1.432 (8)
Rh(2)–C(2)	2.385 (6)		
Bond Angles			
P(1)–Rh(1)–O(1)	90.4 (1)	C(1)–Rh(2)–C(2)	37.7 (2)
P(1)–Rh(1)–C(1)	177.0 (1)	C(1)–Rh(2)–C(12)	96.1 (3)
P(1)–Rh(1)–C(11)	92.1 (2)	C(2)–Rh(2)–C(12)	90.7 (3)
O(1)–Rh(1)–C(1)	87.6 (2)	Rh(1)–O(1)–C(9)	132.4 (4)
O(1)–Rh(1)–C(11)	176.4 (3)	Rh(2)–C(2)–C(9)	127.4 (4)
C(1)–Rh(1)–C(11)	90.0 (3)	Rh(1)–C(1)–Rh(2)	95.4 (2)
P(2)–Rh(2)–O(2)	88.8 (1)	Rh(1)–C(1)–C(2)	173.9 (4)
P(2)–Rh(2)–C(1)	171.7 (1)	Rh(2)–C(1)–C(2)	79.2 (3)
P(2)–Rh(2)–C(2)	153.5 (1)	Rh(2)–C(2)–C(1)	70.1 (3)
P(2)–Rh(2)–C(12)	91.3 (2)	Rh(2)–C(2)–C(3)	120.0 (4)
O(2)–Rh(2)–C(1)	83.8 (2)	C(1)–C(2)–C(3)	169.3 (6)
O(2)–Rh(2)–C(2)	88.5 (2)	Rh(1)–C(11)–O(3)	175.6 (6)
O(2)–Rh(2)–C(12)	90.7 (3)	Rh(2)–C(12)–O(4)	178.1 (6)

alkynes. **7** reacts with phenylacetylene, cyclohexylacetylene, (trimethylsilyl)acetylene, and methyl propiolate to give acetic acid and the compounds $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2R)(CO)_2(PCy_3)_2]$ (R = Ph (**18**), Cy (**19**), Me_3Si (**20**), MeO_2C (**21**)). In contrast, complex **8** is inert toward cyclohexylacetylene, (trimethylsilyl)acetylene, and methyl propiolate, whereas the reaction with phenylacetylene produces a solid that is a 1:1 mixture of $[Rh_2(\mu\text{-}OOCCF_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(CO)_2(PCy_3)_2]$ (**22**) and **8**. The formation of **18–22** can be rationalized in terms of the protonation of one carboxylate ligand in **7** and **8** by the acidic proton of the terminal alkyne. Thus, the lower pK_a of trifluoroacetic acid in comparison to the pK_a of acetic acid could explain the differences observed in reactivity. The same reason could also explain the marked difference in the behavior of these complexes toward pyrazole. Whereas the dimers $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}pz)(CO)_2(PCy_3)_2]$ (**24**) and $[Rh(\mu\text{-}pz)(CO)(PCy_3)]_2$ (**25**) can be obtained from **7** and pyrazole by addition of stoichiometric amounts of the azolate to **7**, the mononuclear compound $[Rh(OCOCF_3)(CO)(Hpz)(PCy_3)]$ (**26**) is produced by reaction of **8** with pyrazole.

Experimental Section

General Data. All reactions were carried out by using standard Schlenk techniques. Solvents were dried and purified by known procedures and distilled prior to use. Elemental analyses were performed with a Perkin-Elmer 240 microanalyzer. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian XL 200 or a Varian UNYT 300 spectrometer. Infrared spectra were run on a Perkin-Elmer 783 spectrophotometer, either as solids (Nujol mulls on polyethylene sheets) or solutions (NaCl cell windows). Molecular weights were determined in chloroform solutions with a Knauer vapor pressure osmometer (isopiestic method). The starting materials $[Rh(\mu\text{-}OOCCH_3)(COD)]_2$ (**1**), $[Rh(\mu\text{-}OOCCF_3)(COD)]_2$ (**2**), $[Rh(\mu\text{-}OOCCH_3)(CO)_2]_2$ (**9**), and $[Rh(\mu\text{-}OOCCF_3)(CO)_2]_2$ (**10**) were prepared by published methods.[3]

Preparation of $[Rh(OCOCH_3)(COD)(PCy_3)]$ (3). A suspension of **1** (100 mg, 0.18 mmol) in 30 mL of hexane was treated with tricyclohexylphosphine (103.8 mg, 0.37 mmol), and the resulting suspension was stirred at room temperature. After 1 h of reaction, the resulting yellow suspension was concentrated under reduced pressure to about 5 mL, and the yellow solid was filtered off, washed with cool hexane, and dried under vacuum; yield 140 mg (71%). Anal. Calcd for $C_{28}H_{48}O_2PRh$: C, 61.01; H, 8.78. Found: C, 61.08; H, 8.63. ^1H NMR ($CDCl_3$): δ 1.2–2.3 (Cy), 1.82 (s, $OCOCH_3$), 2.4 (br, CH_2), 3.65 (br, CH=), 5.53 (br, CH=).

Preparation of $[Rh(OCOCF_3)(COD)(PCy_3)]$ (4). The complex was prepared by using the procedure described for **3**; a suspension of **2** (100 mg, 0.15 mmol) was treated with

tricyclohexylphosphine (86.8 mg, 0.31 mmol) and the resulting yellow solid was filtered off, washed with cool hexane, and dried under vacuum; yield 148 mg (79%). Anal. Calcd for $C_{28}F_3H_{45}O_2PRh$: C, 55.64; H, 7.65. Found: C, 56.00; H, 7.25. ^1H NMR ($CDCl_3$): δ 1.2–2.2 (Cy), 2.4 (br, CH_2), 3.30 (br, CH=), 5.75 (br, CH=).

Preparation of [Rh(OCOCH$_3$)(CO)$_2$(PCy$_3$)] (5). The complex was prepared by bubbling CO through a suspension of **3** (100 mg, 0.18 mmol) in 30 mL of hexane over 10 min. The resulting yellow microcrystalline solid was filtered off, washed with hexane, and dried under vacuum; yield 63 mg (70%). Anal. Calcd for $C_{22}H_{36}O_4PRh$: C, 53.02; H, 7.23. Found: C, 52.70; H, 7.24.

Preparation of [Rh(OCOCF$_3$)(CO)$_2$(PCy$_3$)] (6). The complex was prepared by bubbling CO through a suspension of **4** (100 mg, 0, 17 mmol) in 30 mL of hexane over 10 min. The resulting yellow solid was filtered off, washed with hexane, and dried under vacuum; yield 69 mg (69%). Anal. Calcd for $C_{22}F_3H_{33}O_4PRh$: C, 47.84; H, 5.97. Found: C, 48.40; H, 6.50.

Preparation of [Rh(μ-OOCCH$_3$)(CO)(PCy$_3$)]$_2$ (7). The complex can be prepared by using three different procedures.

(a) A suspension of **9** (260 mg, 0.59 mmol) in 50 mL of hexane was treated with PCy_3 (334 mg, 1.19 mmol), and the mixture was refluxed over 6 h. The resulting red solution was filtered through Kieselguhr, and the filtrate was cooled to room temperature, causing the precipitation of a yellow microcrystalline solid which was filtered off, washed with acetone, and dried under vacuum; yield 370 mg (66%).

(b) A suspension of **5** (100 mg, 0.20 mmol) in 25 mL of hexane was refluxed over 1 h. The resulting yellow solid was filtered off, washed with hexane, and dried under vacuum; yield 42 mg (45%).

(c) A suspension of **11** (100 mg, 0.14 mmol) in 25 mL of hexane was treated with PCy_3 (41 mg, 0.14 mmol) and the mixture refluxed over 1 h. The resulting yellow solid was filtered off, washed with acetone, and dried under vacuum; yield 91 mg (70%). Anal. Calcd for $C_{42}H_{72}O_6P_2Rh_2$: C, 53.62; H, 7.71. Found: C, 54.18; H, 8.36. ^1H NMR ($CDCl_3$): δ 1.2–2.2 (Cy), 1.95 (s, O_2CCH_3). Mol. wt: calcd, 941; found, 969.

Preparation of [Rh(μ-OOCCF$_3$)(CO)(PCy$_3$)]$_2$ (8). The complex was prepared by using the three different procedures described for **7**: (a) starting from **10** (100 mg, 0.23 mmol) and PCy_3 (131 mg, 0.46 mmol), yield 180 mg (75%); (b) starting from **6** (120 mg, 0.21 mmol), yield 46 mg (40%); (c) starting from **12** (130 mg, 0.16 mmol) and PCy_3 (46 mg, 0.16 mmol), yield 134 mg (80%). Anal. Calcd for $C_{42}F_6H_{66}O_6P_2Rh_2$: C, 48.10; H, 6.29. Found: C, 48.17; H, 6.28.

Preparation of [Rh$_2$(μ-OOCCH$_3$)$_2$(CO)$_3$(PCy$_3$)] (11). A suspension of **9** (150 mg, 0.34 mmol) in 10 mL of hexane was treated with tricyclohexylphosphine (96 mg, 0.35 mmol), and the solution was refluxed. After 4 h of reaction, the resulting dark violet solid was filtered off, washed with cool hexane, and dried under vacuum; yield 161 mg (69%). Anal. Calcd for $C_{25}H_{39}O_7PRh$: C, 43.64; H, 5.38. Found: C, 44.00; H, 5.80.

Preparation of [Rh$_2$(μ-OOCCF$_3$)$_2$(CO)$_3$(PCy$_3$)] (12). The complex was prepared using the procedure described for **11** by starting from **10** (100 mg, 0.23 mmol) and PCy_3 (72 mg, 0.25 mmol). The yield of the resulting violet solid was 138 mg (75%). Anal. Calcd for $C_{25}F_6H_{33}O_7PRh_2$: C, 37.70; H, 4.40. Found: C, 37.78; H, 4.27.

Preparation of [Rh$_2$(μ-OOCCH$_3$)$_2$(μ-MeO$_2$CC≡CCO$_2$Me)(CO)$_2$(PCy$_3$)$_2$] (13). A suspension of **7** (100 mg, 0.11 mmol) in 25 mL of hexane was treated with $MeO_2CC{\equiv}CCO_2Me$ (15 μL, 0.12 mmol), and the mixture was refluxed over 6 h. The resulting solution was cooled to room temperature, causing the precipitation of a yellow microcrystalline solid, which was filtered off, washed with acetone, and dried under vacuum; yield 34 mg (25%). Anal. Calcd for $C_{48}H_{78}O_{10}P_2Rh_2$: C, 53.23; H, 7.26. Found: C, 52.72; H, 7.67. ^1H NMR ($CDCl_3$): δ 1.2–2.1 (Cy), 1.85 (s, O_2CCH_3), 3.63 (s, CO_2Me).

Preparation of [Rh$_2$(μ-OOCCF$_3$)$_2$(μ-MeO$_2$CC≡CCO$_2$Me)(CO)$_2$(PCy$_3$)$_2$] (14). The complex was prepared by using the procedure described for **13**; a suspension of **8** (100 mg, 0.09 mmol) was treated with $MeO_2CC{\equiv}CCO_2Me$ (13 μL, 0.10 mmol). The resulting yellow solid was filtered off, washed with acetone, and dried under vacuum; yield 29 mg (27%). Anal. Calcd for $C_{48}F_6H_{72}O_{10}P_2Rh_2$: C, 48.44; H, 6.05. Found: C, 49.05; H, 6.55. ^1H NMR ($CDCl_3$): δ 1.2–2.2 (Cy), 3.63 (s, CO_2Me).

Preparation of [Rh$_2$(μ-OOCCH$_3$)$_2$(μ-MeO$_2$CC≡CCO$_2$Me)(η^2-MeO$_2$CC≡CCO$_2$Me)(CO)$_2$(PCy$_3$)] (15). A suspension of **13** (100 mg, 0.11 mmol) in 35 mL of hexane was treated with $MeO_2CC{\equiv}CCO_2Me$ (31 μL, 0.12 mmol), and the mixture was refluxed over 16 h. The resulting suspension was cooled to room temperature, and the yellow microcrystalline solid was filtered off, washed with cool hexane, and dried under vacuum; yield 80 mg (59%). Anal. Calcd for $C_{36}H_{51}O_{14}PRh_2$: C, 45.78; H, 5.44. Found: C, 45.52; H, 5.55. ^1H NMR ($CDCl_3$): δ 1.2–2.2 (Cy), 1.85 (s, O_2CCH_3), 3.66 (s, CO_2Me), 3.77 (s, CO_2Me), 3.78 (s, CO_2Me), 3.88 (s, CO_2Me).

Preparation of [Rh$_2$(μ-OOCCH$_3$)$_2$(μ-MeO$_2$CC≡CCO$_2$Me)(CO)$_3$(PCy$_3$)] (16). A suspension of **11** (113 mg, 0.16 mmol) in 30 mL of hexane was treated with $MeO_2CC{\equiv}CCO_2Me$ (35 μL, 0.28 mmol), and the reaction mixture was stirred at room temperature. After 12 h of reaction, the resulting yellow suspension was concentrated under reduced pressure to about 5 mL, and the solid was filtered off, washed with acetone, and dried under vacuum; yield 38 mg (28%). Anal. Calcd for $C_{31}H_{45}O_{11}PRh_2$: C, 44.84; H, 5.68. Found: C, 45.20; H, 5.42. ^1H NMR ($CDCl_3$): δ 1.2–2.2 (Cy), 1.85 (s, O_2CCH_3), 3.63 (s, CO_2Me), 3.69 (s, CO_2Me).

Preparation of [Rh$_2$(μ-OOCCF$_3$)$_2$(μ-MeO$_2$CC≡CCO$_2$Me)(CO)$_3$(PCy$_3$)] (17). The complex was prepared by using the procedure described for **16**; a suspension of **12** (150 mg, 0.18 mmol) was treated with $MeO_2CC{\equiv}CCO_2Me$ (23 μL, 0.19 mmol). The resulting yellow solid was filtered off, washed with acetone, and dried under vacuum; yield 29 mg (27%). Anal. Calcd for $C_{31}F_6H_{39}O_{11}PRh_2$: C, 39.66; H, 4.37. Found: C, 39.54; H, 4.36. ^1H NMR (C_6D_6): δ 1.2–2.2 (Cy), 3.23 (s, CO_2Me), 3.53 (s, CO_2Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 194.7 (m, CO), 188.3 (m, CO), 186.3 (m, CO), 172.2 (q, $OCOCF_3$, $^2J_{F-C}$ = 49 Hz), 168.3 (q, $OCOCF_3$, $^2J_{F-C}$ = 40 Hz), 159.5 (s, CO_2Me), 148.4 (s, CO_2Me), 117.4–109.9 (m, C=C), 51.9 (s, OMe), 51.7 (s, OMe), 34.5 (d, CH_2CHP, J_{P-C} = 15 Hz), 28.8 (s, CH_2), 28.7 (s, CH_2), 27.7 (d, CH_2CHP, J_{P-C} = 10 Hz), 27.5 (d, CH_2CHP, J_{P-C} = 11 Hz), 26.0 (s, CH_2).

Preparation of [Rh$_2$(μ-OOCCH$_3$)(μ-η^1:η^2-C$_2$Ph)(CO)$_2$(PCy$_3$)$_2$] (18). A suspension of **7** (100 mg, 0.11 mmol) in 30 mL of acetone was treated with phenylacetylene (11 μL, 0.1 mmol). The mixture was stirred for 1 h, and the resulting yellow suspension was concentrated under reduced pressure to about 5 mL. The solid was filtered off, washed with acetone, and dried under vacuum; yield 66 mg (61%). Anal. Calcd for $C_{48}H_{74}O_4P_2Rh_2$: C, 58.65; H, 7.59. Found: C, 58.65; H, 7.69. ^1H NMR ($CDCl_3$): δ 1.2–2.2 (Cy), 1.78 (s, CO_2Me), 7.5 (m, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 190.3 (dd, CO, J_{Rh-C} = 73.9 Hz, J_{P-C} = 17.4 Hz), 181.1 (s, O_2CCH_3), 132.4 (s, Ph), 128.1 (s, Ph), 127.5 (s, Ph), 125.9 (s, Ph), 58.4 (s, ≡CPh), 34.2 (d, CH_2CHP, J_{P-C} = 20 Hz), 30.1 (s, $OCCH_3$), 27.9 (d, CH_2CHP, J_{Rh-C} = 10 Hz), 27.7 (s, CH_2), 26.5 (s, CH_2).

Preparation of [Rh$_2$(μ-OOCCH$_3$)(μ-η^1:η^2-C$_2$Cy)(CO)$_2$(PCy$_3$)$_2$] (19). A suspension of **7** (150 mg, 0.16 mmol) in 30 mL of acetone was treated with cyclohexylacetylene (20 μL, 0.16 mmol). The mixture was stirred for 6 h, and the resulting orange-yellow suspension was concentrated under reduced pressure to about 10 mL. The solid was filtered off, washed with small quantities of acetone, and dried under vacuum; yield 87 mg (55%). Anal. Calcd for $C_{48}H_{80}O_4P_2Rh_2$: C, 58.30; H, 8.15. Found: C, 57.74; H, 8.58. ^1H NMR (C_6D_6): δ 1.2–2.2 (Cy), 1.91 (s, $OCCH_3$).

Preparation of [Rh$_2$(μ-OOCCH$_3$)(μ-η^1:η^2-C$_2$SiMe$_3$)(CO)$_2$(PCy$_3$)$_2$] (20). A suspension of **7** (150 mg, 0.16 mmol) in 30 mL of acetone was treated with (trimethylsilyl)acetylene (23 μL, 0.16 mmol). The mixture was stirred for 48 h, and the resulting orange solution was stored at −78 °C overnight. The yellow microcrystalline solid was filtered off, repeatedly washed with hexane, and dried under vacuum; yield 92 mg (59%). Anal. Calcd for $C_{45}H_{78}O_4P_2SiRh_2$: C, 55.22; H, 8.03. Found: C, 55.08; H, 8.59.

Table III. Parameters Used in the Extended Hückel Calculations

orbital	H_{ii} (eV)	ξ_1	ξ_2	C_1	C_2
Rh 4d	−12.5	4.29	1.97	0.5807	0.5685
5s	−8.09	2.135			
5p	−4.57	2.10			
P 3s	−18.6	1.6			
3p	−14.0	1.6			
C 2s	−21.4	1.625			
2p	−11.4	1.625			
O 2s	−32.3	2.275			
2p	−14.9	2.275			
H 1s	−13.6	1.3			

Table IV. X-ray Crystal Structure of $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(CO)_2(PCy_3)_2]$ (18)[a]

formula	$C_{48}H_{74}O_4P_2Rh_2$
mol wt	982.87
cryst size	0.25 × 0.25 × 0.4 mm
diffractometer	Enraf-Nonius CAD4
radiation	Mo Kα (0.710 69 Å), graphite monochromator, Zr filter (factor 16.4)
cell constants[b]	a = 16.418 (7) Å b = 15.715 (3) Å c = 20.117 (8) Å α = 90.0° β = 112.92 (2)° γ = 90.0° V = 4780 (3) Å^3
space group	monoclinic, $P2_1/n$ (No. 14), Z = 4, d_{calc} = 1.336 g cm^{-3}, μ = 7.8 cm^{-1}
data collection	T = 293 K, $\omega/2\theta$ scan, max 2θ = 44°, 6376 rflns measd, 6119 unique, 3731 obsd [$F_o > 2\sigma(F_o)$]
cor	Lp cor and empiric abs cor (ψ-scan method, min transmissn 96.77%)
struct soln	Patterson (SHELXS-86)
refinement	full-matrix least squares, 505 params, unit weights, (Enraf-Nonius SDP), R = 0.058, R_w = 0.067
no. of reflns/param	7.39
residual electron density	+0.60/−0.50 e Å^{-3}

[a] All hydrogen positions were calculated according to ideal geometry (d_{C-H} = 0.95 Å) and were used only in structure factor calculations. [b] For 23 reflections (12° < θ < 14°).

^{1}H NMR (C_6D_6): δ 0.57 (s, Me_3Si), 1.2–2.2 (Cy), 1.85 (s, CO_2Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 191.3 (dd, CO, J_{Rh-C} = 75 Hz, J_{P-C} = 17 Hz), 180.9 (s, O_2CCH_3), 34.7 (d, CH_2CHP, J_{P-C} = 19 Hz), 30.5 (s, $OCCH_3$), 28.1 (d, CH_2CHP, J_{P-C} = 11 Hz), 26.8 (s, CH_2), 24.8 (s, CH_2), 1.6 (s, Me_3Si).

Preparation of $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2CO_2Me)(CO)_2(PCy_3)_2]$ (21). A suspension of 7 (150 mg, 0.16 mmol) in 30 mL of acetone was treated with methyl propiolate (15 μL, 0.16 mmol). After the mixture was stirred for 4 h, the resulting orange suspension was filtered off, and the solid was washed with acetone and dried under vacuum; yield 55 mg (54%). Anal. Calcd for $C_{44}H_{72}O_6P_2Rh_2$: C, 54.78; H, 7.52. Found: C, 54.26; H, 7.92. ^{1}H NMR ($CDCl_3$): δ 1.2–2.3 (Cy), 1.84 (s, O_2CMe), 3.46 (s, CO_2Me).

Preparation of $[Rh_2(\mu\text{-}OOCCF_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(CO)_2(PCy_3)_2]$ (22). This compound was prepared analogously to 18, by starting from 8 (105 mg, 0.1 mmol) and phenylacetylene (11 μL, 0.1 mmol). An orange solid was isolated, which from the IR and $^{31}P\{^1H\}$ NMR spectra turned out to be a mixture of 8 and 22 in the ratio 1:1. Attempts to separate the two complexes by fractional crystallization or chromatographic techniques failed.

Preparation of $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(COD)_2]$ (23). A suspension of 1 (750 mg, 1.39 mmol) in 30 mL of acetone was treated with phenylacetylene (228 μL, 2.2 mmol). After the mixture was stirred for 20 min at room temperature, the resulting yellow suspension was cooled to −78 °C. The red-orange solid was filtered off, washed with hexane, and dried under vacuum; yield 150 mg (19%). Anal. Calcd for $C_{28}H_{32}O_2Rh_2$: C, 53.62; H, 5.53. Found: C, 53.75; H, 5.55. ^{1}H NMR (C_6D_6): δ 1.8 (br, 8 H, CH_2), 1.87 (s, 3 H, O_2CMe), 2.4 (br, 8 H, CH_2), 4.12 (br, 4H, =CH), 4.91 (br, 4 H, =CH), 7.94 (br, 5 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 182.5 (s, O_2CCH_3), 132.7 (s, Ph), 128.6 (s, Ph), 127.9 (s, Ph), 126.8 (s, Ph), 90.7 (d, =CH, J_{Rh-C} = 10 Hz), 80.9 (d, =CH, J_{Rh-C} = 10 Hz), 78.7 (d, =CH, J_{Rh-C} = 14 Hz), 73.2 (d, =CH, J_{Rh-C} = 11 Hz), 58.4 (s, ≡CPh), 32.3 (CH_2), 30.8 (s, CH_3), 27.9 (s, CH_2), 28.0 (s, CH_2), 24.0 (s, CH_2).

Table V. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2
Rh(1)	0.36888 (6)	0.17759 (7)	0.15606 (5)	3.13 (2)
Rh(2)	0.38332 (6)	0.24980 (7)	0.01344 (5)	3.08 (2)
P(1)	0.2487 (2)	0.141 (2)	0.1781 (2)	3.12 (7)
P(2)	0.2908 (2)	0.2574 (2)	−0.1055 (1)	2.87 (7)
O(1)	0.3666 (5)	0.0709 (6)	0.0934 (4)	4.3 (2)
O(2)	0.3958 (5)	0.1194 (5)	0.0008 (4)	3.6 (2)
O(3)	0.3894 (8)	0.3267 (9)	0.2482 (7)	11.9 (4)
O(4)	0.3723 (8)	0.4342 (7)	0.0317 (6)	8.0 (4)
C(1)	0.4685 (7)	0.2224 (8)	0.1317 (5)	3.3 (3)
C(2)	0.5254 (7)	0.2475 (9)	0.1100 (6)	3.8 (3)
C(3)	0.6025 (8)	0.2691 (9)	0.0969 (6)	4.5 (3)
C(4)	0.6155 (9)	0.347 (1)	0.0719 (8)	6.4 (4)
C(5)	0.6900 (9)	0.364 (1)	0.0599 (9)	7.8 (5)
C(6)	0.7544 (9)	0.306 (1)	0.0727 (9)	9.1 (5)
C(7)	0.7443 (8)	0.228 (1)	0.0971 (8)	7.1 (5)
C(8)	0.6667 (9)	0.207 (1)	0.1080 (7)	5.3 (4)
C(9)	0.3870 (7)	0.0604 (8)	0.0397 (6)	3.2 (3)
C(10)	0.4031 (9)	−0.0289 (9)	0.0228 (7)	5.7 (4)
C(11)	0.3781 (9)	0.267 (1)	0.2119 (7)	6.4 (4)
C(12)	0.3750 (8)	0.3631 (9)	0.0241 (7)	4.7 (4)
C(13)	0.1487 (7)	0.1929 (8)	0.1434 (5)	3.2 (3)
C(14)	0.1252 (8)	0.2116 (8)	0.0635 (6)	3.8 (3)
C(15)	0.0412 (9)	0.2648 (9)	0.0334 (7)	4.8 (4)
C(16)	0.0455 (9)	0.345 (1)	0.0762 (8)	5.6 (4)
C(17)	0.0712 (9)	0.3285 (8)	0.1542 (7)	5.1 (4)
C(18)	0.1571 (8)	0.2752 (8)	0.1866 (6)	3.8 (3)
C(19)	0.2098 (7)	0.0233 (8)	0.1300 (6)	3.3 (3)
C(20)	0.2730 (7)	−0.0505 (8)	0.1649 (6)	3.4 (3)
C(21)	0.2560 (7)	−0.1267 (9)	0.1148 (7)	4.2 (3)
C(22)	0.1606 (9)	−0.1569 (8)	0.0947 (8)	5.1 (4)
C(23)	0.0936 (8)	−0.0850 (9)	0.0645 (8)	4.7 (4)
C(24)	0.1154 (8)	−0.0073 (8)	0.1134 (8)	4.6 (4)
C(25)	0.2673 (8)	0.1128 (9)	0.2755 (6)	4.3 (3)
C(26)	0.3536 (9)	0.074 (1)	0.3214 (7)	5.7 (4)
C(27)	0.3715 (8)	0.0818 (9)	0.4025 (6)	4.3 (3)
C(28)	0.295 (1)	0.045 (1)	0.4175 (7)	6.2 (4)
C(29)	0.210 (1)	0.079 (1)	0.3725 (8)	7.7 (5)
C(30)	0.1917 (8)	0.0716 (9)	0.2911 (7)	4.6 (3)
C(31)	0.3588 (7)	0.2596 (8)	−0.1609 (5)	3.3 (3)
C(32)	0.4146 (8)	0.3407 (8)	−0.1457 (7)	4.4 (3)
C(33)	0.4714 (8)	0.343 (1)	−0.1898 (7)	5.6 (3)
C(34)	0.5303 (8)	0.267 (1)	−0.1760 (7)	5.5 (4)
C(35)	0.4744 (8)	0.1851 (9)	−0.1931 (6)	4.7 (3)
C(36)	0.4177 (8)	0.1802 (8)	−0.1483 (6)	4.3 (3)
C(37)	0.2198 (7)	0.3538 (8)	−0.1358 (6)	3.3 (3)
C(38)	0.1507 (7)	0.3601 (9)	−0.1018 (6)	4.0 (3)
C(39)	0.1062 (8)	0.4482 (9)	−0.1181 (8)	5.1 (4)
C(40)	0.0684 (9)	0.4671 (9)	−0.1972 (8)	5.3 (4)
C(41)	0.1365 (9)	0.4605 (9)	−0.2320 (8)	5.2 (4)
C(42)	0.1785 (8)	0.3716 (9)	−0.2162 (6)	4.2 (3)
C(43)	0.2254 (7)	0.1590 (8)	−0.1343 (5)	3.3 (3)
C(44)	0.165 (1)	0.1492 (9)	−0.2162 (7)	5.2 (4)

Preparation of $[Rh_2(\mu\text{-}OOCCH_3)(\mu\text{-}pz)(CO)_2(PCy_3)_2]$ (24). A suspension of 7 (100 mg, 0.11 mmol) in 30 mL of acetone was treated with pyrazole (7.0 mg, 0.1 mmol), and the mixture was stirred for 1 h. A yellow suspension was obtained, which was filtered off, and the yellow solid was washed with acetone and dried under vacuum; yield 55 mg (54%). Anal. Calcd for $C_{43}H_{72}N_2O_4P_2Rh_2$: C, 54.43; H, 7.65; N, 2.95. Found: C, 54.40; H, 7.85; N, 2.75. ^{1}H NMR ($CDCl_3$): δ 1.2–2.2 (Cy), 1.76 (s, O_2CMe), 6.13 (br, pz), 7.25 (br, pz), 7.54 (br, pz). Mol wt: calcd, 948; found, 862.

Preparation of [Rh(pz)(CO)(PCy$_3$)]$_2$ (25). A suspension of 7 (100 mg, 0.11 mmol) in 30 mL of acetone was treated with pyrazole (14.0 mg, 0.2 mmol). After the mixture was stirred for 1 h, the resulting yellow suspension was filtered off, and the solid was washed with acetone and dried under vacuum. Recrystallization of this residue from CH_2Cl_2/acetone gave a yellow microcrystalline solid, yield 85 mg (83%). Anal. Calcd for $C_{44}H_{72}N_4O_2P_2Rh$: C, 55.23; H, 7.58; N, 5.85. Found: C, 54.97; H, 7.58; N, 5.23. ^{1}H NMR ($CDCl_3$): δ 1.2–2.2 (Cy), 6.03 (br, pz), 7.31 (br, pz), 7.46 (br, pz). Mol wt: calcd, 956; found, 1082.

Preparation of [Rh(OCOCF$_3$)(CO)(Hpz)(PCy$_3$)] (26). A suspension of 8 (130 mg, 0.12 mmol) in 30 mL of acetone was treated with pyrazole (17.7 mg, 0.26 mmol), and the mixture was stirred for 1 h. A yellow suspension was obtained, which was filtered off, and the yellow solid was washed with acetone and dried under vacuum; yield 71 mg (50%). Anal. Calcd for $C_{24}H_{37}N_2O_3PRh$: C, 48.66; H, 6.25; N, 4.73. Found: C, 49.06; H, 6.56; N, 4.90. ^{1}H NMR (C_6D_6): δ 1.2–2.2 (Cy), 5.61 (br, pz), 6.38 (br, pz), 7.44 (br, pz), 13.75 (s, NH).

Molecular Orbital Calculations. Extended Hückel[20] molecular orbital calculations were performed using the modified Wolfsberg–Helmholtz formula[21] and the program CACAO.[22] The H_{ii} and orbital exponents are listed in Table III and were used as supplied by the program. The structural parameters were taken from the molecular structure of 18 and standard parameters[23] for the model compound [Rh$_2$(μ-OOCH)(μ-η^1:η^2-C$_2$H)(CO)$_2$(PCy$_3$)$_2$]. In the symmetric bridging mode of the alkynyl ligand a Rh–C distance of 3.116 Å was used. The angle between the carbon at the carboxylate ligand, the midpoint Rh–Rh, and the bridging carbon atom at the alkynyl ligand was set to 90°. A uniform variation in the structural parameters was assumed for intermediate geometries.

X-ray Data Collection. Crystals of compound 18 suitable for X-ray diffraction studies were obtained by the slow diffusion of acetone into a saturated benzene solution of the compound. Crystal data collection parameters are summarized in Table IV. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied (ψ-scan method, minimum transmission 96.77%). The structure was solved using the Patterson method (SHELXS-86)[24] in order to obtain the fractional coordinates of the two rhodium atoms. All other calculations were performed using the program package SDP[25] from Enraf-Nonius. The positions of the remaining non-hydrogen atoms were located in subsequent difference-Fourier syntheses. Atomic coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined with full-matrix least squares (Table V). The positions of all hydrogen atoms were calculated according to ideal geometry and were included only in structure-factor calculation.

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Supplementary Material Available: Tables of hydrogen atom positional parameters and their estimated standard deviations, bond lengths and angles, general anisotropic displacement parameter expressions (U's), and refined displacement parameter expressions (β's) (12 pages). Ordering information is given on any current masthead page.

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