Inorg. Chem. **1980**, *19*, 1571–1575

processes and that an NH_3 group is lost by the remaining $Fe_2(NH_2)_2^+$ ion (cf. Table I). The strength of the amide bridges in the complex is also indicated by the fact that $Fe_2(NO)_4(NH_2)_2$ is not cleaved by nitric oxide under ambient conditions whereas the corresponding halo dimers, $[Fe(NO)_2X]_2$, readily convert to $Fe(NO)_3X$ in the presence of NO.

It is likely that the diamido complex was first prepared in 1960 by reaction[30] 15 although at that time both the starting

$$Fe_2(CO)_6(NH_2)_2 + 4NO \xrightarrow{\text{benzene}} Fe_2(NO)_4(NH_2)_2 + 6CO \quad (15)$$

material and product were incorrectly formulated as $Fe_2(CO)_6(NH)_2$ and $Fe_2(NO)_4(NH)_2$, respectively. Subsequent X-ray and mass spectrometric studies of the carbonyl reactant established its true identity and led the investigators to suggest that the nitrosyl product of reaction 15 is also probably a diamido species.[31] Our comparison of the spectral properties displayed by an authentic sample of $Fe_2(NO)_4(NH_2)_2$ with those reported for "$Fe_2(NO)_4(NH)_2$" supports such a view.

For both the chromium amido complexes described in section d and $Fe_2(NO)_4(NH_2)_2$, we have found no evidence for the interconversion of NO and NH_2 ligands. However, unlike for $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)_2$, we have observed that the iron dimer does react further with I to produce as yet unidentified nitrosyl-containing products. Further studies of this and related reactions with carbanions are currently in progress.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of a grant (A5885) to P.L. and a predoctoral fellowship to B.W.H.

Registry No. I, 22722-98-1; $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_3)$, 73199-26-5; $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, 36607-01-9; $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$, 68013-60-5; $[(\eta^5\text{-}C_5H_5)Cr(NO)_2(CO)]PF_6$, 69439-82-3; $(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$, 68013-59-2; $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$, 53504-57-7; $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]BF_4$, 73199-25-4; $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I$, 69120-55-4; $[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$, 12193-64-5; $(\eta^5\text{-}CH_3C_5H_4)Mn(NO)(PPh_3)I$, 69120-58-7; $(\eta^5\text{-}CH_3C_5H_4)Mn(NO)(PPh_3)H$, 73199-24-3; $(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$, 66795-25-3; $[(\eta^5\text{-}C_5H_5)Co(NO)]_2$, 51862-20-5; $(\eta^5\text{-}C_5H_5)W(NO)I_2[P(OPh)_3]$, 73199-12-9; $(\eta^5\text{-}C_5H_5)Co(NO)I$, 33114-12-4; $(\eta^5\text{-}C_5H_5)W(NO)(H)(I)[P(OPh)_3]$, 73199-23-2; $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$, 71341-43-0; $[(\eta^5\text{-}C_5H_5)W(NO)H(I)]_2$, 73199-22-1; $[(\eta^5\text{-}C_5H_5)Mo(NO)I]_2$, 37368-74-4; $[(\eta^5\text{-}C_5H_5)Mo(NO)I_2]_2$, 12203-25-7; $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)_2$, 57673-35-5; $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_3(NH_2)$, 39722-97-9; $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, 12071-51-1; $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)(OH)$, 73199-21-0; $[Fe(NO)_2Cl]_2$, 21576-91-0; $Fe_2(NO)_4(NH_2)_2$, 73199-20-9; $Fe(NO)_3Cl$, 14972-71-5.

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and the Istituto d'Chimica Inorganica ed Generale, Universita di Torino, Turin, Italy

Regiospecific Substitution of Trialkylphosphines for Carbon Monoxide in Hydridoorganoruthenium Clusters

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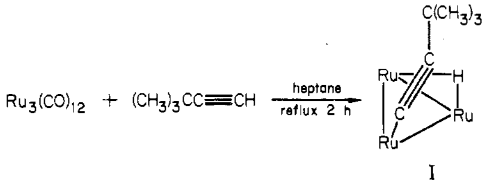
and ENRICO SAPPA

Received June 11, 1979

The reaction of two structural types of hydridoorganoruthenium clusters $HRu_3(CO)_9(C_6H_9)$ (I) and $HRu_3(CO)_9(C_5H_7)$ (IIa, IIb) with triphenylphosphine and trimethyl phosphite have been studied. The major product for both structural types is a monophosphine derivative (I → III; IIa → V; IIb → VI) in which a carbonyl group has been replaced only on ruthenium atoms having a σ bond with the organic ligand. Solution structures are assigned on the basis of variable-temperature ^{13}C and ^1H NMR studies. In III, only conformers with the phosphine ligand in a radial position are populated from −80 to +40 °C. However, axial–radial carbonyl exchange at the substituted ruthenium atom occurs at about the same rate as in I. A bis(phosphine) derivative of I has also been isolated and characterized (IV).

Introduction

Synthetic routes to a variety of organometallic derivatives of $Ru_3(CO)_{12}$ make possible systematic investigations of the chemistry of an organic molecule bound to a trimetallic site.[1] In the case of *tert*-butylacetylene, μ_2-hydrido-$\mu_1\sigma^1,\mu_2\pi^4$-(*tert*-butylacetylido)-triruthenium nonacarbonyl (I) is isolated in 80% yield[2] (eq 1). This reaction is general for acetylenes

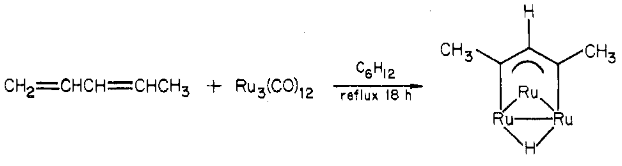


(1)

I

with bulky, functionalized groups α to the triple bond where yields of 50–60% are obtained.[3]

A variety of dienes yield single trimetallic products when reacted with $Ru_3(CO)_{12}$, and construction of isomeric organometal derivatives with systematic structural variations is now possible. Both isoprene and 1,3-pentadiene give μ_2-hydrido-1,3-di-$\mu_1\sigma^1,\mu_2\pi^3$-allyl complexes in 35 and 50% yields, respectively[4] (eq 2a and 2b). An inspection of the solid-state



IIa

(2a)

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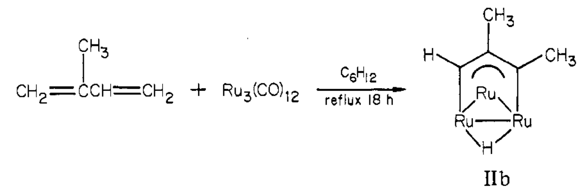

IIb

(2b)

structural data available for I[5] and analogues of II[6] reveals some interesting parallels and contrasts (see Figure 1). In both I and II: (1) the metal–carbon σ bonds are 0.20–0.25 Å shorter than the π bonds; (2) the organic ligand has undergone C–H bond scission to form a five-electron donor from a four; (3) the sixth electron (required for replacement of three carbonyls) is provided by a bridging hydride.

A few dinuclear complexes of the type $Fe_2(CO)_6(\text{-}C{\equiv}CR)(\mu_2\text{-}PR_2)$ show regiospecific substitution of PR_3 for CO at the metal atom σ bonded to the acetylene.[7,8] We report here the results of a comparative study of phosphine substitution in the organotriruthenium clusters I and II.

Results and Discussion

The reaction of I with either equimolar or excess PR_3 (R = C_6H_5, OCH_3) was examined at 80 °C (cyclohexane) and 110 °C (toluene). At both temperatures two trimetallic products are obtained in the same relative yields (eq 3).

$$\underset{\text{I}}{HRu_3(CO)_9(C_6H_9)} + PR_3 \rightarrow \underset{\text{III (40–50\%)}}{HRu_3(CO)_8(C_6H_9)(PR_3)} + \underset{\text{IV (10–20\%)}}{HRu_3(CO)_7(C_6H_9)(PR_3)_2} \quad (3)$$

Approximately 10% of I is recovered, and a third phosphine-containing compound is formed but could not be isolated in sufficient yield for characterization.

Assignment of the solution structure of III was made by analysis of the variable-temperature ^{13}C NMR by using a 10–15% ^{13}CO enriched sample. We recently reported the V.T. ^{13}C NMR of I.[9] A localized axial-radial CO site exchange at Ru(3) (Figure 1) is observed as the lowest energy independent CO-scrambling process ($\Delta G^{\ddagger} = 13.2 \pm 0.5$ kcal/mol[10]). As the temperature is raised, axial–radial exchange at Ru(1) and Ru(2) begins and overlaps with the onset of total CO scrambling probably via CO-bridged intermediates ($\Delta G^{\ddagger} \geq 15.6 \pm 0.5$ kcal/mol) as has been noted for many substituted transition-metal–carbonyl clusters.[11,12]

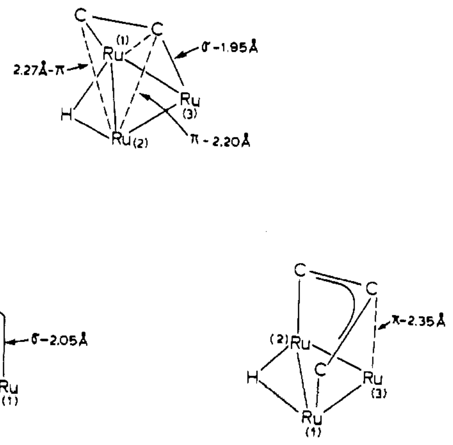

Figure 1. Structural data for $HRu_3(CO)_9(C_6H_7)$ (I) and $HRu_3(CO)_3(RCCR'CR'')$ (IIa and IIb).

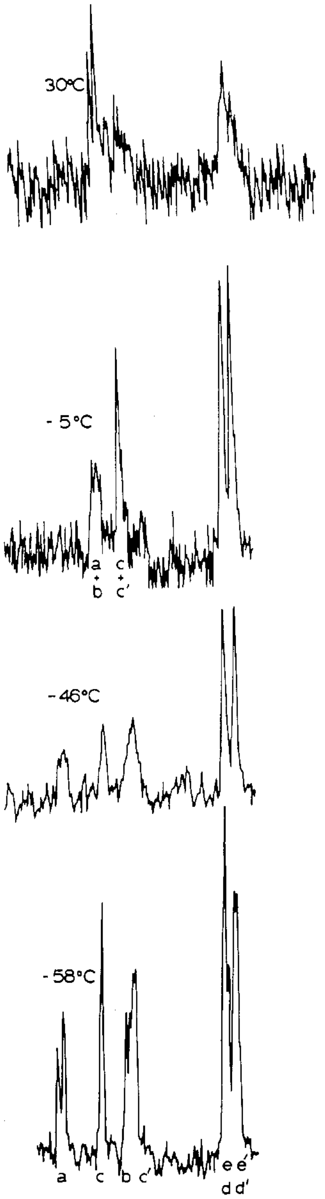

Figure 2. Variable-temperature ^{13}C NMR spectra in the CO region of $HRu_3(CO)_8(C_6H_9)P(C_6H_5)_3$ (III) from −58 to +40 °C.

The low-temperature limiting spectrum of III observed at −58 °C (Figure 2) is consistent only with a single conformer with the phosphine substituted at Ru(3) and in a radial position. The overall averaging pattern of the CO resonances and a comparison of the relative chemical shifts and integrated intensities of III with I lead logically to the following assignments (Scheme I and Figure 2). Resonance a at 206.3

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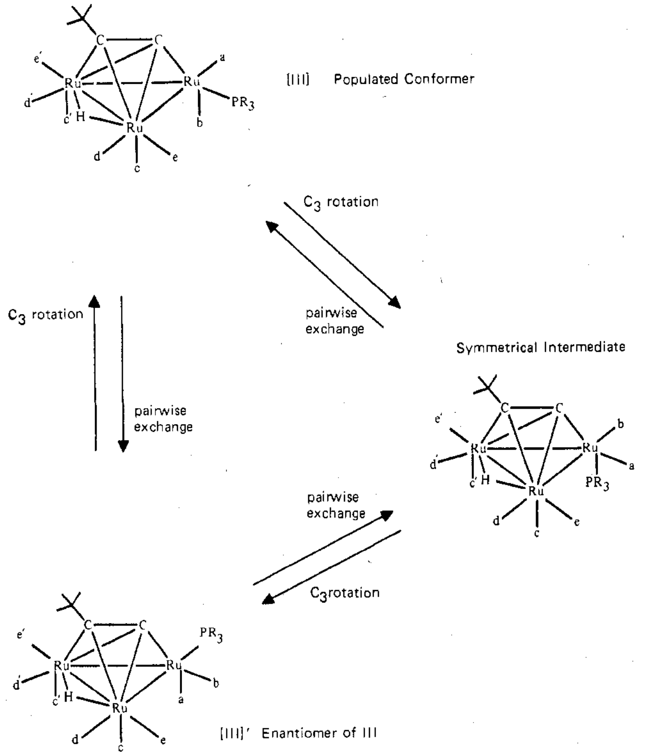
(10) D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 256 (1971).

(11) This proposed mechanism for total carbonyl scrambling in I cannot be distinguished from rotation of the organic ligand coupled with axial–radial exchange. An examination of the ^{13}C NMR of the C(1) acetylido carbon of III in the high-temperature limit is in progress. Preservation of $^2J(PC)$ coupling would validate the mechanism proposed herein. Our present ^{13}C NMR data for III are aimed only at assignment of the solution structure.

(12) S. Aime and L. Milone, *Prog. Nucl. Magn. Reson. Spectrosc.*, **11** (1977).

Scheme I. Pathways for Axial-Radial Exchange at Ru(3) of III

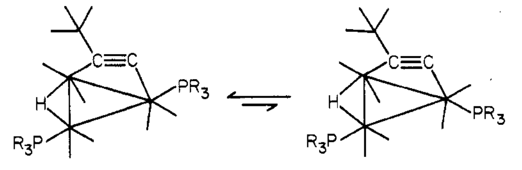


ppm (^2J(PC) = 11.3 Hz, relative intensity = 1) is assigned to the axial CO on Ru(3) on the basis that in I and in this type of complex in general the axial ^{13}CO shift given is always downfield of radial CO shift at a given metal atom.[13] Resonance b, the radial CO on Ru(3) at 199.9 ppm (^2J(PC) = 8.9 Hz, relative intensity = 1), averages with a as the temperature is increased to −5 °C by axial–radial site exchange of $(CO)_a$, $(CO)_b$, and the phosphine ligand. This process simultaneously averages resonance c at 202.4 ppm (relative intensity = 1) with c′ at 199.4 ppm (^2J(PC) = 4.7 Hz, relative intensity = 1), which we assign to the axial carbonyl groups $(CO)_c$ and $(CO)_{c'}$ on Ru(1) and Ru(2). The group of partially overlapping resonances at 189.8–191.0 ppm (relative intensity = 4) collapses to two resonances on going from −58 to −30 °C. This arises from the averaging of $(CO)_d$ with $(CO)_{d'}$ and $(CO)_e$ with $(CO)_{e'}$ on Ru(1) and Ru(2) by axial–radial site exchange at Ru(3). The localized exchange at Ru(3) restores a twofold plane of symmetry but does not average $(CO)_d$, $(CO)_e$, and $(CO)_c$ on Ru(1) with each other or the corresponding CO groups on Ru(2). As the temperature is increased to +40 °C, resonances a and b ($(CO)_a$ and $(CO)_b$) average to a sharp doublet at 203.1 ppm (^2J(PC) = 10.1 Hz) while resonances dd′, ee′, and cc′ begin to broaden and coalesce, indicating the onset of axial–radial exchange at Ru(1) and Ru(2).[11]

We have estimated $\Delta G^{\ddagger}$ for axial–radial exchange at Ru(3) to be 11.8 ± 0.5 kcal/mol[10] by using a coalescence temperature of −30 °C. This is slightly lower than the corresponding barrier in I, suggesting that steric factors (i.e., substitution of a large $P(C_6H_5)_3$ group) are relatively unimportant in axial–radial exchange at Ru(3).

Variable-temperature ^{1}H NMR from −60 to +40 °C of III and its $P(OCH_3)_3$ analogue show doublets in the μ_2-hydride region[1] at δ −21.3 and −21.4, respectively, with a ^3J(PH) = 2.4 Hz. That the value of this coupling does not change throughout the temperature range examined and that ^2J(PC) at Ru(3) averages to the exact average of $^2J(P-(CO)_b)$ and $^2J(P-(CO)_a)$ at the low-temperature limit indicate that there is no appreciable population of the more crowded axial isomer in the temperature range examined. This is consistent with what is found to date for other phosphine substituted clusters.[13]

Using the knowledge gained from our ^{1}H–^{13}C NMR investigation case R = OCH_3 able to partially define the solution structure of the bis(phosphine) derivatives IV, $HRu_3(CO)_7TBA[PR_3]_2$ (R = C_6H_5, OCH_3). At −60 °C in CD_2Cl_2 a doublet of doublets at δ −21.4 (^2J(PH) = 10.0 Hz, ^3J(PH) = 2.5 Hz) is observed. Partially overlapping with this doublet of doublets is a second broadened doublet at δ −21.7 (R = C_6H_5; δ −21.1 for R = OCH_3). The relative integrated intensity of the small doublet is approximately 0.2 of the larger doublet of doublets and has a ^2J(PH) = 10 Hz. As the temperature is increased, the small doublet merges with the larger doublet of doublets. We interpret the dynamic behavior in the hydride region of IV in terms of an equilibrium between IVa and IVb.



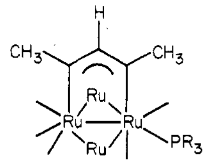
IVa 4:1 IVb

In both the case R = C_6H_5 and the case R = OCH_3 two *tert*-butyl methyl resonances in about a 4:1 ratio are observed at −60 °C, which coalesce to a single resonance as the temperature is raised. Increasing the temperature from −30 (or −20) to +40 ° results in further broadening of the doublet of doublets to an ill-defined broad band which is undoubtedly due to the onset of a–r exchange at Ru(1) and Ru(2). Although we cannot definitively assign the location of phosphine to the radial position syn to the hydride bridge, we feel this assignment is reasonable on the basis of analogy with phosphine-substituted osmium hydrides.[13]

The reaction of II with $P(C_6H_5)_3$ in cyclohexane yields only one product in addition to nonspecific cluster degradation (eq 4).

$$\underset{\text{IIa}}{HRu_3(C_5H_7)(CO)_9} + P(C_6H_5)_3 \xrightarrow[\text{reflux 3 h}]{C_6H_{12}} \underset{\text{V}}{HRu_3(CO)_8(C_5H_7)P(C_6H_5)_3} \quad (4)$$

The ^{1}H NMR of IIa in the hydride region shows a doublet at δ −19.0 (^4J(HH) = 2.0 Hz) which has been shown to arise from long-range coupling between the central allylic hydrogen and the hydride.[4] Compound V shows a doublet of doublets centered at δ 19.4 (^2J(PH) = 14.0 Hz, ^4J(HH) = 3.0 Hz). The formerly equivalent methyls are nonequivalent in V with one appearing as a doublet (^4J(PH) = 4.0 Hz). These data lead to assignment of the structure of V as



V

The reaction of the unsymmetrical isomer IIb with triphenylphosphine in cyclohexane at 80 °C leads to the isolation of one product band by TLC. ^{1}H NMR analysis however showed this to be an approximately 3:2 mixture of two positional isomers VIa and VIb (eq 5), whose structure can be readily assigned on the following basis: (1) two doublets in the hydride region δ −19.5 (J(PH) = 14.0 Hz) and δ −19.6 (J(PH) = 14.0 Hz) in a 3:2 ratio, (2) the observation of two

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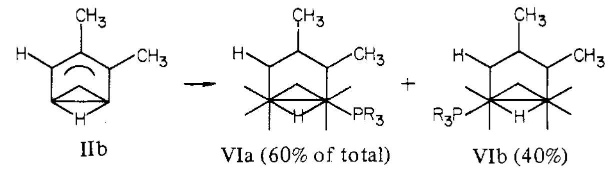
(13) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 2397 (1977).



(5)

singlet resonances for the terminal hydrogen resonances in a 3:2 ratio at δ 8.55 and 7.95, respectively, and (3) two terminal methyl resonances, a singlet and a doublet with shifts almost identical with those of the analogous methyls in V (Table I). ^{13}C NMR studies of IIa and IIb have been reported and show that carbonyls are static on the NMR time scale at Ru(1) and Ru(2).[12]

Conclusions

It is clear from these results that substitution of PR_3 for CO is favored at the Ru atoms having σ bonds to the organic ligand, regardless of the location of the hydride ligand. This regiospecificity may arise from kinetic or thermodynamic factors. The σ-bonded carbons may labilize CO dissociation, which is the rate-determining step in phosphine substitution in these compounds. However, it would seem that the more rapid intermetallic CO-scrambling process would randomize vacant sites on the cluster in the $HRu_3(CO)_8(L)$ intermediate. On the other hand, differences in local metal atom electron density could make one substitution product more thermodynamically stable than the other. We are currently investigating the reactivity of these compounds to elucidate these points further.

Experimental Section

All analytical and spectral data are summarized in Table I.

Materials. $Ru_3(CO)_{12}$ was synthesized by known procedures from $RuCl_3{\cdot}(1\text{–}3)H_2O$ (Mathey-Bishop). All solvents were dried over molecular sieves, and all reactions were carried out under an atmosphere of prepurified nitrogen.

Spectra. ^{1}H and ^{13}C NMR spectra were measured in CD_2Cl_2 which was used as the internal reference (δ 5.23). Variable-temperature ^{1}H NMR spectra were measured on a Varian XL-100 spectrometer operating in the Fourier transform mode (20-μs pulse width, 4-s repetition rate, 10K data points), and room-temperature spectra were measured on a Varian EM-360. ^{13}C NMR spectra were measured on a 10–15% ^{13}CO-enriched sample (as determined by mass spectroscopy) in the presence of 0.03 M $Cr(acac)_3$ on a Bruker HFX-10 spectrometer operating in the Fourier transform mode (10-μs pulse width, 1–2-s repetition rate, 8K data points). Temperature measurements were calibrated with a thermometer in a sample tube (±1 °C).

Preparation of I.[14] A 1.5-g (2.4-mmol) sample of $Ru_3(CO)_{12}$, 1.5 mL (15 mmol) of $(CH_3)_3CC{\equiv}CH$ and 600 mL of heptane were combined under nitrogen and refluxed for 2 h. The solution was evaporated to dryness and then washed with small portions of cold diethyl ether, yielding pure yellow crystals of I (1.1–1.30 g (70–80%)). The compound was usually recrystallized from heptane at −20 °C before further use.

Preparation of IIa and IIb.[16] A 0.500-g (0.83-mmol) sample of $Ru_3(CO)_{12}$, 4.0 mL (40 mmol) of isoprene or 4.0 mL (40 mmol) of 1,3-pentadiene, and 600 mL of cyclohexane were combined in a 2.0-L three-necked flask and refluxed for 12–18 h. The reaction mixture was evaporated to dryness and purified by dry-column chromatography by using grade III activity silica gel and hexane as the eluant. A single orange band was extracted with methylene chloride and crystallized from heptane at −20 °C (yield of IIa 212 mg (44%), yield of IIb 121 mg (25%)).

Reaction of I with $(C_6H_5)_3P$ or $(CH_3O)_3P$. A 318-mg (0.5-mmol) sample of I, 135 mg of $(C_6H_5)_3P$ (0.5 mmol) or 0.06 mL of $(CH_3O)_3P$ (0.5 mmol), and 50 mL of cyclohexane or toluene were combined in a 100-mL three-necked flask and refluxed with magnetic stirring for

Table I. Analytical and Spectroscopic Data

no.	compd	% C[a]		% H[a]		mass spec:[b] M⁺		IR:[c] ν_{CO}	^{1}H NMR (rel intens)[d]			
		calcd	found	calcd	found	calcd	found		δ(CH_3)	δ(R)	δ(CH)	δ(hydride)
III	$HRu_3(CO)_8(C_6H_9)P(R)_3$											
	$R = C_6H_5$	44.13	44.00	2.89	2.85	871.70	872	2090 s, 2070 s, 2010 s, 1995 s, 1955 sh	1.3 s (9)	7.3–7.7 m (15)		−21.2 d (1); ^3J(PH) = 2.5 Hz
	$R = OCH_3$	27.83	27.86	2.62	2.81	733.58	734	2050 m, 2000 s, 1980 m, 1955 s, 1940 m	1.4 s (9)	3.7 d (9); ^2J(PH) = 13 Hz		−21.5 d (1); ^3J(PH) = 2.5 Hz
IV	$HRu_3(CO)_7(C_6H_9)(PR_3)_2$											
	$R = C_6H_5$	53.21	53.07	3.83	3.87	1105.96	1106	2050 s, 2005 s, 1985 s, 1950 m, 1930 m, 1920 m	1.4 s (9)	7.3–7.7 m (30)		−21.5 m (1)
	$R = OCH_3$	27.14	27.50	3.55	3.35	829.56	830	2080 m, 2050 s, 2010 s, 1995 s, 1975 m, 1950 m	1.3 s (9)	3.7 d (18); J(PH) = 13 Hz		−21.5 m (1)
V	$HRu_3(CO)_8(C_5H_7)P(C_6H_5)_3$	43.40	43.31	2.70	2.82	857.6	857.0	2070 s, 2030 s, 2010 s, 1990 s, 1980 s, 1935	2.7 s (3), 2.1 d (3); ^4J(PH) = 4 Hz	7.2–7.5 m (5)	6.55 (1); J(HH) = 2.0 Hz	−19.3; ^4J(HH) = 2.0 Hz, ^2J(PH) = 14.0 Hz
VI	$HRu_3(CO)_8(C_5H_7)P(C_6H_5)_3$	43.40	42.91	2.70	2.77	857.60	857	2030 s, 2005 s, 1980 s, 1965 s, 1950 s, 1865 w	2.75 s (1.2), 2.75 s (1.2), 2.10 d (1.8); ^4J(PH) = 4 Hz	7.2–7.4 m (15)	8.55 s (0.6), 7.95 s (0.4)	−19.6 d (0.6), −19.5 d (0.4); ^2J(PH) = 14 Hz

[a] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories. [b] Parent ions reported are based on ^{101}Ru. $M^+ - 28$ fragments, (ligand)$Ru_3(CO)_n^+$ from $n = 4$ to 9. [c] KBr disk on a Beckman Aculab infrared spectrometer; ν_{CO} values are ±10 cm^{-1}. [d] Reported downfield positive from tetramethylsilane, ±0.05 ppm; coupling constants are ±0.5 Hz. Letters following δ values indicate multiplicity, and numbers in parentheses are integrated relative intensities, ±5%. δ(CH) is internal allylic proton in IIa and terminal allylic proton in IIb.

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(14) Preparations presented here are modified from ref 2 and 4. Spectral data are in accord with those reported for I, IIa, and IIb.

2–3 h. The reaction mixture was evaporated to dryness, the solid was taken up in methylene chloride, and the products were separated by thin-layer chromatography on silica gel by using 1:19 ether–hexane as eluant. For R = C_6H_5, five to six bands were separated: (1) unreacted I, 10–15%, (2) unreacted phosphine, (3) III, 210–240 mg (40–55%), (4) IV, 50–60 mg (10–15%), (5) pale yellow band in a trace amount not identified, and (6) red band (toluene reaction only) also in trace amounts not identified. (Yields given are on bands extracted with CH_2Cl_2.) Products III and IV were recrystallized from heptane. Similar yields are obtained by using this procedure for R = OCH_3.

Reaction of IIa with $(C_6H_5)_3P$. A 150-mg (0.241-mmol) sample of IIa, 65 mg (0.248 mmol) of $(C_6H_5)_3P$, and 175 mL of cyclohexane were combined in a 250-mL three-necked flask and refluxed with magnetic stirring for 2 h. The reaction mixture was evaporated to dryness, the solid was taken up in dichloromethane, and the products were separated by TLC on silica gel by using 1:9 ether–hexanes as eluant. Four bands were separated: (1) unreacted IIa, 5 mg, (2) V, 65 mg (31.4% yield), (3) orange band in a trace amount not identified, and (4) yellow-orange band, 8 mg, not identified (yields given on bands extracted with CH_2Cl_2). Product V was recrystallized from ether–heptane at −20 °C.

Reaction of IIb with $(C_6H_5)_3P$. A 60-mg (0.096-mmol) sample of IIb, 25 mg (0.096 mmol) of $(C_6H_5)_3P$, and 60 mL of cyclohexane were combined in a 100-mL three-necked flask and refluxed with magnetic stirring for 2 h. The reaction mixture was evaporated to dryness, the solid was taken up in methylene chloride, and the components were separated by TLC on silica gel by using 8% ether in hexanes as eluant. Five bands were separated: (1) unreacted IIb, 7 mg, (2) VI, 20 mg (24% yield), (3) orange band in a trace amount not identified, (4) yellow band in a trace amount not identified, and (5) reddish orange band in a trace amount not identified (yields given on bands extracted with CH_2Cl_2). Product VI was recrystallized from chloroform–hexanes at −20 °C.

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Registry No. I, 57673-31-1; IIa, 56943-13-6; IIb, 57327-10-3; III (R = C_6H_5), 72582-02-6; III (R = OCH_3), 72582-03-7; IV (R = C_6H_5), 72582-04-8; IV (R = OCH_3), 72599-26-9; V, 72708-35-1; VIa, 72582-05-9; VIb, 72582-06-0; $Ru_3(CO)_{12}$, 15243-33-1; $(CH_3)_3CC\equiv CH$, 917-92-0; isoprene, 78-79-5; 1,3-pentadiene, 504-60-9.

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η^3-β-Diketonato(2−) Complexes of Palladium(II)

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The palladium(II) complexes containing dianions of acetylacetone and ethyl acetoacetate, [Pd(acac(2−)-C^1–C^3)(NN)] and [Pd(etac(2−)-C^1–C^3)(NN)], where NN is 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, or 1,10-phenanthroline, have been prepared by the reactions of the corresponding terminal-carbon-bonded complexes of the β-dicarbonyl compounds with thallium(I) acetylacetonate as a base. The η^3 coordination of the β-diketonate dianions in these complexes was confirmed by analytical, IR, and NMR measurements.

The η^3 carbon-bonded complex of acetylacetone with palladium(II) [PdCl(acac-C^1–C^3)]$_2$ (**1**) was prepared by the reaction of dichlorobis(benzonitrile)palladium(II) with acetylacetone in acetone at room temperature and reacted with 2,2′-bipyridine to afford the η^1 complex [PdCl(acac-C^1)(bpy)] (**3a**).[1] Similarly the η^3 palladium(II) complex of ethyl acetoacetate [PdCl(etac-C^1–C^3)]$_2$ (**2**) was obtained from the ethanolysis of diketene in the presence of the tetrachloropalladate(II) and was also prepared by the direct reaction of palladium(II) chloride with the keto ester.[2] The bridge-splitting reaction of **2** with 2,2′-bipyridine yielded [PdCl(etac-C^1)(bpy)] (**4a**).[3]

The acetylacetone terminal carbon bonded to palladium(II) in **3a** still contains the ionizable methylene protons, and it reacted with other metal compounds to produce the dinuclear and trinuclear complexes in which the acetylacetonate dianion is working as a C,O,O′-bridging ligand.[4] It was supposed that thallium(I) acetylacetonate might displace the chloride ion in **1** and **2** to produce the palladium(II) complexes containing two kinds of unidentate β-diketonate anions, one the terminal carbon bonded and the other the central carbon bonded or otherwise oxygen bonded. In fact the reactions occurred easily at room temperature, but contrary to expectation, the products were the palladium(II) complexes containing the β-diketonate dianion. This paper reports on these novel types of complexes.

Experimental Section

η^3 Complexes of Monoanions of Acetylacetone and Ethyl Acetoacetate with Palladium(II). Di-μ-chloro-bis(η^3-1-acetyl-2-hydroxyallyl)dipalladium(II), [PdCl(acac-C^1–C^3)]$_2$ (**1**), was prepared by the reported method.[1] Di-μ-chloro-bis(η^3-1-ethoxycarbonyl-2-hydroxyallyl)dipalladium(II), [PdCl(etac-C^1–C^3)]$_2$ (**2**), was prepared by the following method originally proposed by Tezuka.[2] Ethyl acetoacetate (10 mL) was added with stirring to a suspension of palladium(II) chloride (1.10 g, 6.20 mmol) in water (80 mL) at 70 °C. A brown precipitate appeared promptly, which was filtered after 1 h of stirring, washed with water until the washings were no longer colored, and dried in vacuo. The filtrate combined with the washings was left standing at room temperature for 9 days to deposit another crop of the product which showed the same IR spectrum as that of the above precipitate. The total yield of the crude product was 1.42 g (85%), which was dissolved in hot benzene. After filtration, the solution was

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