15, 122116-37-4; **16**, 32985-20-9; **17**, 68183-88-0; **18**, 122116-38-5; **20**, 122116-43-2; **21**, 122116-44-3; **22**, 122116-39-6; **23**, 122116-40-9; **24**, 122116-41-0; acetophenone, 98-86-2; ethylene, 74-85-1; 1-hexene, 592-41-6; 1-phenyl-1-(trimethylsiloxy)ethene, 13735-81-4; benzonitrile, 100-47-0; (trimethylsilyl)acetylene, 1066-54-2.

Supplementary Material Available: Tables of crystal data, atomic coordinates, thermal parameters, and selected interatomic distances and angles for **24** (6 pages); a listing of observed and calculated structure factors for **24** (18 pages). Ordering information is given on any current masthead page.

Preparation, Properties, and Reactions of Metal-Containing Heterocycles. 65.[1] The Behavior of Tetracarbonyl(η^2-ethene)ruthenium toward Activated Alkenes and Alkynes

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$(\eta^2\text{-}C_2H_4)Ru(CO)_4$ (**1**) reacts with the activated olefins $R^1R^2C{=}CR^2R^1$ (**2a,b**) (**a**, R^1 = H, R^2 = CN; **b**, $R^1 = R^2$ = CN) to give the substitution products $(\eta^2\text{-}R^1R^2C{=}CR^2R^1)Ru(CO)_4$ (**3a,b**). Toward electron-poor alkynes, however, **1** is a suitable educt for different cyclization reactions. Under elimination of carbon monoxide and ethylene, **1** reacts with two alkyne molecules $ZC{\equiv}CZ$ (**4c,d**) (**c**, Z = CO_2CH_3; **d**, Z = $CO_2C_2H_5$) to form the tricyclic compounds **8c,d** containing two tricarbonylruthenacyclopentadiene rings. This reaction proceeds via nondetectable intermediates $(\eta^2\text{-}ZC{\equiv}CZ)_2Ru(CO)_3$ (**5c,d**) and $(OC)_3\overline{RuCZ{=}CZCZ{=}C}Z$ (**7c,d**). The empty coordination sites at the ruthenium atoms are occupied by two ester carbonyl donor bonds in each case. The dimeric structure of **8d**, showing an eight-membered ring in a chair conformation, was elucidated by an X-ray structural analysis. **8d** crystallizes in the monoclinic space group $P2_1/c$ with Z = 2. The cell dimensions are a = 13.101 (3) Å, b = 17.768 (4) Å, c = 9.536 (3) Å, and β = 96.43 (3)°. **8c,d** are catalysts for the cyclotrimerization of the alkynes **4c,d**. The turnover numbers for the formation of the benzenehexacarboxylic acid hexaalkyl esters **13c,d** are on the order of 200 h^{-1}. Both Ru–O bonds in **8c,d** are cleaved by carbon monoxide resulting in the formation of the ruthenacyclopentadienes $(OC)_4\overline{RuCZ{=}CZCZ{=}C}Z$ (**10c,d**). In contrast to the reaction of **1** with the alkynes **4c,d**, the action of hexafluoro-2-butyne (**4e**) on **1** affords the heterocycle **9e** which, on the basis of spectroscopical data, can be described as a ruthenabicyclo[3.2.0]heptene.

Introduction

Carbonyl olefin complexes of the iron triad transition metals constitute an important area of investigation from both the synthetic[2a] and theoretical[2b] point of view. For the simplest species $(\eta^2\text{-ethene})M(CO)_4$ (M = Fe, Ru, Os) only two general methods of preparation are described. The groups of Wrighton,[3a] Takats,[3b] and Grevels[3c] investigated successfully the photochemical synthesis and the photochemistry of these compounds. Alternatively, the nucleophilic elimination cycloaddition method on ethane-1,2-diylbis(trifluoromethanesulfonate) with the $[M(CO)_4]^{2-}$ anions offers a very simple route to tetracarbonyl(η^2-ethene)metal complexes of iron,[4a] ruthenium,[4b] and osmium.[1] These compounds should be excellent starting materials for ligand exchange reactions[5] with other olefins and for C–C coupling reactions with alkenes or alkynes.[6] Form our own work we know that the η^2-ethene–ruthenium bond in $(\eta^2\text{-}C_2H_4)Ru(CO)_4$ (**1**) is very labile.[4b] The photochemistry of **1** shows that one or two CO ligands are substituted by the corresponding number of ethene molecules.[3a] Both results suggest that tetracarbonyl(η^2-ethene)ruthenium (**1**) should be a source of interesting reactions. Here we report the behavior of **1** toward activated alkenes and different substituted alkynes, depending on the reaction conditions.

Experimental Section

General Procedures. All preparations were carried out under an atmosphere of purified argon. n-Hexane, n-pentane, chloroform, acetonitrile, and acetone were rendered water- and oxygen-free by distillation from $LiAlH_4$ and K_2CO_3. Instrumentation: mass spectra, Varian MAT 711 A; IR, Bruker FT-IR spectrometers, Models IFS 113c and IFS 48; ^1H, $^{13}C\{^1H\}$ NMR, Bruker AC 80 and Bruker Cryospec WM 400 at 80.13, 20.15 and 400, 100.62 MHz, respectively; ^{19}F NMR, Bruker WP 80 at 75.26 MHz, internal standard C_6F_6 relative to $FCCl_3$. Elemental analyses were carried out with Carlo Erba Model 1106 and Perkin-Elmer Model 4000 atomic absorption spectrometers. A molecular weight determination was carried out with Knauer Dampfdruckosmometer. Research grade C_2H_4 was obtained from Messer-Griesheim. Tetracyanoethylene, fumaric acid dinitrile, and acetylenedicarboxylic acid dimethyl and diethyl esters were obtained from Merck Schuchardt. Hexafluoro-2-butyne was obtained from

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Strem Chemicals. $(\eta^2\text{-}C_2H_4)Ru(CO)_4$ was prepared either by our method[7] or via a photochemical procedure.[3a]

Tetracarbonyl(η^2-dicyanoethylene)ruthenium (3a). To a vigorously stirred ethene-saturated solution of 1 (450 mg, 0.19 mmol) in 150 mL of *n*-hexane was added in one portion 148 mg (0.19 mmol) of fumaric acid dinitrile (**2a**). After 5 min a white solid precipitated at 20 °C. The solid was filtered (P3) and dried under reduced pressure. Recrystallization from *n*-hexane/acetone yielded pure, colorless **3a** (440 mg, 82%). **3a** dissolves well in polar organic solvents: mp 87 °C dec; IR [$\nu(C\equiv N)$ (KBR, cm^{-1})] 2219 (m), 2217 (m), [$\nu(C\equiv O)$ (KBr, cm^{-1})] 2145 (s), 2066 (vs), 2045 (vs), 2025 (s); ^{1}H NMR (80.13 MHz, $CDCl_3$, 303 K) δ 2.70 (s, CH); $^{13}C\{^1H\}$ NMR (20.15 MHz, acetone-d_6, 303 K) δ 191.75 (s, CO), 189.62 (s, CO), 123.83 (s, CN), 11.17 (s, CH); MS (70 eV), *m/e* (relative intensity, relative to ^{102}Ru) 264 (8, M$^+$ − CO), 236 (9, M$^+$ − 2 CO), 208 (6, M$^+$ − 3 CO), 180 (7, M$^+$ − 4 CO), 78 (100, M$^+$ − $Ru(CO)_4$). Anal. Calcd for $C_8H_2N_2O_4Ru$: C, 33.00; H, 0.69; N, 9.62; Ru, 37.71. Found: C, 33.04; H, 0.71; N, 9.37; Ru, 38.20.

Tetracarbonyl(η^2-tetracyanoethylene)ruthenium (3b). To a vigorously stirred ethene-saturated solution of 1 (450 mg, 0.19 mmol) in 150 mL of *n*-hexane was added in one portion 270 mg (0.19 mmol) of tetracyanoethylene (**2b**). After 30 min a brown solid precipitated at 20 °C. The solid was filtered (P3) and dried under reduced pressure. Recrystallization from acetonitrile/*n*-hexane yielded pure, colorless **3b** (454 mg, 70%). **3b** dissolves well in polar organic solvents: mp 98 °C dec; IR [$\nu(C\equiv N)$ (KBr, cm^{-1})] 2239 (m), 2230 (m), [$\nu(C\equiv O)$ (KBr, cm^{-1})] 2171 (s), 2125 (s), 2101 (vs), 2087 (s); $^{13}C\{^1H\}$ NMR (100.62 MHz, acetone-d_6, 303 K) δ 185.77 (s, CO), 184.34 (s, CO), 116.36 (s, CN), 69.94 (s, C=C); MS (70 eV), *m/e* (relative intensity, relative to ^{102}Ru) 286 (6, M$^+$ − 2 CO), 214 (4, M$^+$ − $(CN)_4C_2$), 128 (100, M$^+$ − $Ru(CO)_4$). Anal. Calcd for $C_{10}N_4O_4Ru$: C, 35.20; N, 16.42; Ru, 29.64. Found: C, 35.60; N, 16.72; Ru, 29.28.

General Preparation of the Heterocycles 8c,d. To a vigorously stirred ethene-saturated soluion of 1 in 200 mL of *n*-hexane was added rapidly 2 equiv of the corresponding acetylenedicarboxylic acid dialkyl ester **4c,d**. At 20 °C a pale yellow solid precipitated after a few minutes. After half the solvent was removed under reduced pressure, the solid was filtered (P3) and dried in vacuo. Recrystallization from acetone/*n*-hexane yielded pure, air-stable, and colorless compounds **8c,d** which dissolves easily in polar organic solvents.

1,1,1,8,8,8-Hexacarbonyl-3,10-dimethoxy-2,9-dioxa-1,8-diruthenatricyclo[9.6.0.0^{4,8}]tetradeca-2,4,6,9,11,13-hexaene-5,6,7,12,13,14-hexacarboxylic Acid Hexamethyl Ester (8c). 1 (450 mg, 0.19 mmol) and acetylenedicarboxylic acid dimethyl ester (**4c**) (532 mg, 0.36 mmol) were reacted: yield 760 mg (85%); mp 185 °C dec; IR [$\nu(C\equiv O)$ (KBr, cm^{-1})] 2112 (vs), 2060 (vs), 2019 (s), [$\nu(>C=O)$ (KBr, cm^{-1})] 1733 (m), 1731 (m), 1694 (m), 1636 (m); ^{1}H NMR (80 MHz, $CDCl_3$, 303 K) δ 3.86 (s, OCH_3), 3.83 (s, OCH_3), 3.73 (s, OCH_3), 3.72 (s, OCH_3); $^{13}C\{^1H\}$ NMR (100.62 MHz, acetone-d_6, 303 K) δ 197.17 (s, RuCO), 194.71 (s, RuCO), 194.71 (s, RuCO), 194.19 (s, RuCO), 190.84 (s, RuCO), 190.24 (s, RuCO), 176.29 (s, OCO), 174.93 (s, OCO) 169.95 (s, OCO), 168.75 (s, OCO), 165.72 (s, OCO), 165.27 (s, OCO), 163.42 (s, OCO), 149.18 (s, OCO), 56.40 (s, OCH_3), 54.73 (s, OCH_3), 51.39 (s, OCH_3), 51.19 (s, OCH_3); MS (FAB, 30 °C), *m/e* (relative intensity, relative to ^{102}Ru) 940 (4, M$^+$), 912 (12, M$^+$ − CO), 884 (20, M$^+$ − 2 CO), 856 (36, M$^+$ − 3 CO), 828 (57, M$^+$ − 4 CO), 800 (66, M$^+$ − 5 CO), 772 (23, M$^+$ − 6 CO). Anal. Calcd for $C_{30}H_{24}O_{22}Ru_2$: C, 38.39; H, 2.57; Ru, 21.52. Found: C, 38.50; H, 2.80; Ru, 21.80.

1,1,1,8,8,8-Hexacarbonyl-3,10-diethoxy-2,9-dioxa-1,8-diruthenatricyclo[9.6.0.0^{4,8}]tetradeca-2,4,6,9,11,13-hexaene-5,6,7,12,13,14-hexacarboxylic Acid Hexaethyl Ester (8d). 1 (450 mg, 0.19 mmol) and acetylenedicarboxylic acid dimethyl ester (**4d**) (646 mg, 0.36 mmol) were reacted: yield 818 mg (82%); mp 148 °C dec; IR [$\nu(C\equiv O)$ (KBr, cm^{-1})] 2113 (s), 2056 (s), 2029 (vs), [$\nu(>C=O)$ (KBr, cm^{-1})] 1718 (m), 1716 (m, sh), 1697 (m), 1631 (m); ^{1}H NMR (80 MHz, $CDCl_3$, 303 K) δ 1.26 (m, OCH_3), 4.22 (m, OCH_2); $^{13}C\{^1H\}$ NMR (100.62 MHz, acetone-d_6, 303 K) δ 194.98 (s, RuCO), 193.27 (s, RuCO), 190.30 (s, RuCO), 189.98 (s, RuCO), 188.64 (s, RuCO), 187.13 (s, RuCO), 174.76 (s, OCO), 168.88 (s, OCO), 164.65 (s, OCO), 164.41 (s, OCO), 163.42 (s, OCO), 162.85 (s, OCO), 149.34 (s, OCO), 146.60 (s, OCO), 65.35 (s, OCH_2), 61.33 (s, OCH_2), 60.37 (s, OCH_2), 60.29 (s, OCH_2), 60.22 (s, OCH_2), 14.37 (s, CH_3), 14.26 (s, CH_3), 14.14 (s, CH_3), 14.03 (s, CH_3); MS (FAB, 30 °C), *m/e* (relative intensity, relative to ^{102}Ru) 1052 (2, M$^+$), 1009 (10, M$^+$ − CO − CH_3), 996 (7, M$^+$ − 2 CO), 981 (12, M$^+$ − CH_3 − 2 CO), 968 (7, M$^+$ − 3 CO), 953 (14, M$^+$ − CH_3 − 3 CO), 940 (18, M$^+$ − 4 CO), 925 (25, M$^+$ − CH_3 − 4 CO), 912 (14, M$^+$ − 5 CO), 894 (52, M$^+$ − 6 CO). Anal. Calcd for $C_{38}H_{40}O_{22}Ru_2$: C, 43.43; H, 3.83; Ru, 19.23. Found: C, 43.43; H, 3.88; Ru, 19.80.

2,2,2,2-Tetracarbonyl-1,5,6,7-tetrakis(trifluoromethyl)-2-ruthenabicyclo[3.2.0]hept-6-ene (9e). At −80 °C ca. 5 mL of hexafluoro-2-butyne (**4e**) was condensed into a well-stirred ethene-saturated solution of **1** in 200 mL of *n*-pentane. The solution was allowed to warm to room temperature while **4e** was bubbled through the solution. After 12 h 1 disappeared (monitored by IR) and the mixture was cooled to −50 °C. After an additional 12 h a white solid precipitated, which was filtered (P3) and washed twice with 10 mL of cold *n*-pentane and dried under reduced pressure to yield 650 mg (78%) of pure, colorless **9e**, which dissolves well in common organic solvents: mp 101 °C dec; IR [$\nu(C\equiv O)$ (*n*-hexane, cm^{-1})] 2157 (w), 2100 (m), 2088 (vs), 2070 (s), [$\nu(C=C)$ (KBr, cm^{-1})] 1653 (w), [$\nu(CF_3)$ (KBr, cm^{-1})] 1343 (m), 1148 (s); ^{1}H NMR (400 MHz, C_6D_6, 303 K) δ 0.61 (m, $^2J_{HH}$ = −10.9, $^3J_{HH}$ = 6.4, $^3J_{HH}$ = 6.9 Hz, 1 H, $RuCHHCH_2$), 0.71 (m, $^3J_{HH}$ = 6.4, $^3J_{HH}$ = 7.3, $^2J_{HH}$ = −10.1, $^4J_{FH}$ = 1.85 Hz, 1 H, $RuCH_2CHH$), 1.22 (m, $^2J_{HH}$ = −10.9, $^3J_{HH}$ = 7.3, $^3J_{HH}$ = 7.2 Hz, 1 H, $RuCHHCH_2$), 1.48 (m, $^3J_{HH}$ = 6.9, $^3J_{HH}$ = 7.2, $^2J_{HH}$ = −10.1, $^4J_{FH}$ = 2.32 Hz, 1 H, $RuCH_2CHH$); $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 303 K) δ 186.38 (q, $^5J_{FC}$ = 0.04 Hz, CO), 185.39 (m, CO), 185.05 (s, CO), 140.13, 136.99 (m, $=CCF_3$), 128.27 (q, $^1J_{FC}$ = 283.8 Hz, CF_3), 126.70 (q, $^1J_{FC}$ = 276.5 Hz, CF_3), 123.64 (q, $^1J_{FC}$ = 273.0 Hz, CF_3), 117.73 (q, $^1J_{FC}$ = 283.0 Hz, CF_3), 30.08, 22.68 (m, CCF_3), 14.22 (m, $RuCH_2CH_2$), 10.78 (s, $RuCH_2CH_2$); ^{19}F NMR (C_6D_6, 303 K) δ −64.53 (m, F_3C), −62.39 (m, F_3C), −55.1 (m, F_3C); MS (FAB, 30 °C), *m/e* (relative intensity, relative to ^{102}Ru) 552 (19, M$^+$ − CH_2), 538 (26, M$^+$ − CO), 496 (54, M$^+$ − CF_3), 482 (31, M$^+$ − 3 CO), 454 (30, M$^+$ − 4 CO); molecular weight determination calcd for $C_{14}H_4F_{12}O_4Ru$ 562.2, found 569.0. Anal. Calcd for $C_{14}H_4F_{12}O_4Ru$: C, 31.01; H, 0.78; F, 40.33; Ru, 17.88. Found: C, 31.57; H, 1.04; F, 39.83; Ru, 18.05.

Reaction of 8c,d with 4c,d. To 30 mg (0.03 mmol) of **8c,d** were added 2.0 mL (16.3 mmol) and 2.5 mL (15.6 mmol) of **4c** and **4d**, respectively. The mixture was slowly warmed up to 80 (**8c**) or 110 °C (**8d**). At this temperature spontaneous polymerization took place. After 10 min 10 mL of diethyl ether and 5 mL of 2 N hydrochloric acid were added to the mixture. The ether phase was separated, washed twice with water, and dried over anhydrous silica. Removal of the solvent under reduced pressure yielded the crude product. **13c** was recrystallized from methanol, and **13d** was purified by filtration (P3) over basic alumina. Yields were quantitative. The compounds were identified by their IR, mass, and ^{1}H NMR spectra.

Benzenehexacarboxylic Acid Hexamethyl Ester (13c): yield 2.29 g (98%); mp 188 °C (lit.[8] mp 192 °C); IR [$\nu(>C=O)$ (KBr, cm^{-1})] 1726; ^{1}H NMR (80 MHz, $CDCl_3$, 303 K) δ 3.88 (s, OCH_3) (lit.[8] δ 3.88); MS (70 eV), *m/e* (relative intensity) 426 (2, M$^+$), 395 (100, M$^+$ − OCH_3).

Benzenehexacarboxylic Acid Hexaethyl Ester (13d): yield 2.60 g (97%); mp 38 °C; IR [$\nu(>C=O)$ (KBr, cm^{-1})] 1739; ^{1}H NMR (80 MHz, $CDCl_3$, 303 K) δ 4.31 (q, OCH_2CH_3) (lit.[9] δ 4.40), 1.33 (t, OCH_2CH_3 (lit.[8] δ 1.46); MS (70 eV), *m/e* (relative intensity) 510 (3, M$^+$), 465 (62, M$^+$ − OC_2H_5), 391 (79, 465 − OC_2H_5 − C_2H_5), 289 (100, 391 − 3 CO − $C(O)OC_2H_5$).

Reaction of 8c,d with CO. At 40 °C a solution of **8c** (235 mg, 0.25 mmol) or of **8d** (262 mg, 0.25 mmol) in 5 mL of acetone was stirred for 12 h under an atmosphere of CO (5 bar). After the solvent was removed under reduced pressure, the residue was stirred with 5 mL of diethyl ether. Removal of the solvent under reduced pressure yielded pale yellow and colorless **10c** and **10d**, respectively. **10c,d** dissolves well in polar organic solvents.

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement of 8d

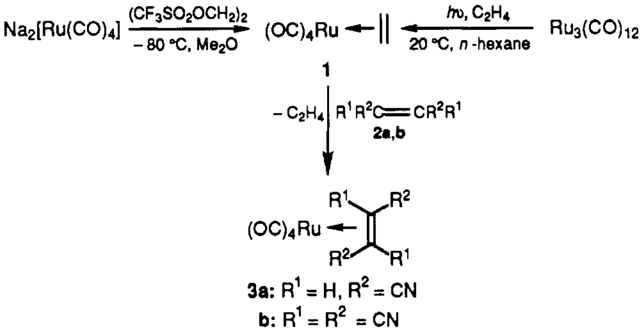
formula	$C_{38}H_{40}O_{22}Ru_2$
fw	1050.87
space group	$P2_1/c$
a, Å	13.101 (3)
b, Å	17.768 (4)
c, Å	9.536 (3)
β, deg	96.43 (3)
V, Å^3	2205.8
Z	2
d_{calcd}, g cm^{-3}	1.582
T, °C	−70
$F(000)$, e	1064
μ(Mo Kα), cm^{-1}	7.492
radiatn (graphite monochromator, λ = 0.709 30 Å)	Mo Kα
θ limits, deg	3–24
scan type	ω/θ
max scan time, s	40
h,k,l range	$0 \rightarrow 10$, $0 \rightarrow 20$, $-15 \rightarrow 15$
reflectns measd	3794
no. of unique data with $I \geq 3\sigma(I)$	2673
no. of variables	280
R	0.034
R_w	0.038
weighting scheme	$w^{-1} = \sigma^2(F)$

1,1,1,1-Tetracarbonyl-1-ruthenacyclopenta-2,4-diene-2,3,4,5-tetracarboxylic Acid Tetramethyl Ester (10c): yield 200 mg (75%); mp 93 °C dec; IR [ν(C≡O) (KBr, cm^{-1})] 2153 (m), 2098 (s), 2085 (s), 2071 (vs), [ν(>C=O) (KBr, cm^{-1})] 1722 (m), 1706 (m); ^{1}H NMR (80 MHz, $CDCl_3$, 303 K) δ 3.78 (s, OCH_3), 3.73 (s, OCH_3); $^{13}C\{^1H\}$ NMR (20.115 MHz, $CDCl_3$, 303 K) δ 186.50 (s, CO), 185.63 (s, CO), 172.47 (s, OCO), 163.72 (s, OCO), 51.93 (s, OCH_3), 51.83 (s, OCH_3); FDMS (8 kV), m/e (relative to ^{102}Ru) 498 (M$^+$). Anal. Calcd for $C_{16}H_{12}O_{12}Ru$: C, 38.64; H, 2.43; Ru, 20.32. Found: C, 38.14; H, 2.26; Ru, 19.94.

1,1,1,1-Tetracarbonyl-1-ruthenacyclopenta-2,4-diene-2,3,4,5-tetracarboxylic Acid Tetraethyl Ester (10d): yield 200 mg (82.6%); mp 83 °C dec; IR [ν(C≡O) (KBr, cm^{-1})] 2156 (m), 2112 (s), 2083 (vs), 2070 (vs), [ν(>C=O) (KBr, cm^{-1})] 1713 (m); ^{1}H NMR (80 MHz, $CDCl_3$, 303 K) δ 4.24 (q, $^3J_{HH}$ = 6.9 Hz, OCH_2CH_3), 4.20 (q, $^3J_{HH}$ = 6.9 Hz, OCH_2CH_3), 1.32 (t, $^3J_{HH}$ = 6.9 Hz, OCH_2CH_3), 1.28 (t, $^3J_{HH}$ = 6.9 Hz, OCH_2CH_3); $^{13}C\{^1H\}$ NMR (20.115 MHz, $CDCl_3$, 303 K) δ 186.70 (s, CO), 185.88 (s, CO), 172.21 (s, OCO), 163.29 (s, OCO), 60.61 (s, OCH_2CH_3), 14.02 (s, OCH_2CH_3), 13.86 (s, OCH_2CH_3); FDMS (8 kV), m/e (relative to ^{102}Ru) 556 (M$^+$). Anal. Calcd for $C_{20}H_{20}O_{12}Ru$: C, 43.32; H, 3.63; Ru, 18.23. Found: C, 43.38; H, 4.01; Ru, 18.52.

X-ray Structure Determination of 8d. Colorless crystals of **8d** were obtained by crystallization from acetone/n-hexane. A suitable crystal with approximate dimensions 0.15 × 0.2 × 0.2 mm was mounted on a glass fiber and then transferred to an Enraf-Nonius CAD-4 diffractometer. The lattice constants were determined with 25 precisely centered high-angle reflections. The final cell parameters and specific data collection parameters for **8d** are summarized in Table I. A study on the diffractometer indicated a monoclinic crystal system, and systematic absences are consistent only with the space group $P2_1/c$ (No. 14). The usual corrections for Lorentz and polarization effects were applied to the intensity data. No decay in the intensities of three standard reflections was observed. The structure was solved by standard Patterson methods,[9] and difference Fourier syntheses[10] were used to locate the remaining non-hydrogen atoms. The DIFABS[11] method of absorption correction was applied after isotropic refinement of all non-hydrogen atoms. All non-hydrogen atoms have anisotropic thermal parameters. The hydrogen atoms were placed at calculated positions and included in the structure factor calculation. The atomic scattering factors used were those from Cromer and Waber.[12]

Scheme I



Results and Discussion

At 20 °C tetracarbonyl(η^2-ethene)ruthenium (**1**) reacts in ethene-saturated solutions of n-hexane with furmaric acid dinitrile (**2a**) and tetracyanoethylene (**2b**). Exchange of the ligand gives the colorless (η^2-alkene)ruthenium complexes **3a,b**, which are well soluble in polar organic solvents (Scheme I). The compounds have been characterized by IR, mass, and ^{1}H and $^{13}C\{^1H\}$ NMR spectra and elemental analyses. In the 5-μm region of the IR spectra of **3a,b** four absorptions for terminal CO groups appear, indicating the C_{2v} symmetry of these complexes. Due to the electron-withdrawing effect of the nitrile groups all CO bands in **3a,b** are shifted to higher wavenumbers compared to those for **1**.

The $^{13}C\{^1H\}$ NMR spectra of **3a,b** show two singlets in the carbonyl range as well as a singlet for the C atoms of the nitrile groups and for the C atoms of the C=C double bonds. In the electron-impact mass spectra of **3a,b** no molecular peaks are detected. The highest mass units, which can be observed, are M$^+$ − CO for **3a** and M$^+$ − 2 CO for **3b**.

Both reactions are examples of the facile exchange of ethene in **1** in the presence of activated alkenes. Hitherto this type of compound was only synthesized by photochemical methods.[3c] The remarkably mild reaction conditions and the excellent yields of **3a,b** offer this ligand exchange reaction as an alternative to the common method of synthesis.

In contrast to the above-mentioned results **1** reacts with acetylenedicarboxylic acid dimethyl ester (**4c**) or diethyl ester (**4d**) at 20 °C with the formation of the heterocycles **8c,d** (Scheme II). Their IR spectra show only three strong absorptions in the region of terminal CO groups. In **8c,d**, due to the end-on coordination of two of the ester carbonyl groups in positions 4 and 9 of the metallacyclopentadiene moieties, a characteristic band appears at ca. 1630 cm^{-1}.[13] This represents a shift to lower wavenumbers compared to the situation in noncoordinated esters.

Because of the low volatility of the tricyclic systems **8c,d** only the FAB method can be used to find the molecular peaks. All six CO ligands are eliminated stepwise. The isotopic distribution of the observed peaks in the mass spectra of **8c,d** are typical for dimeric ruthenium compounds.

In the $^{13}C\{^1H\}$ NMR spectra of **8c,d** six and eight singlets are observed for carbon monoxide ligands and for ester carbonyl carbon atoms, respectively, pointing to highly asymmetric conformation of the heterocycles **8c,d**.

In conformity with similar reactions described in the literature,[14] we propose the following reaction course for

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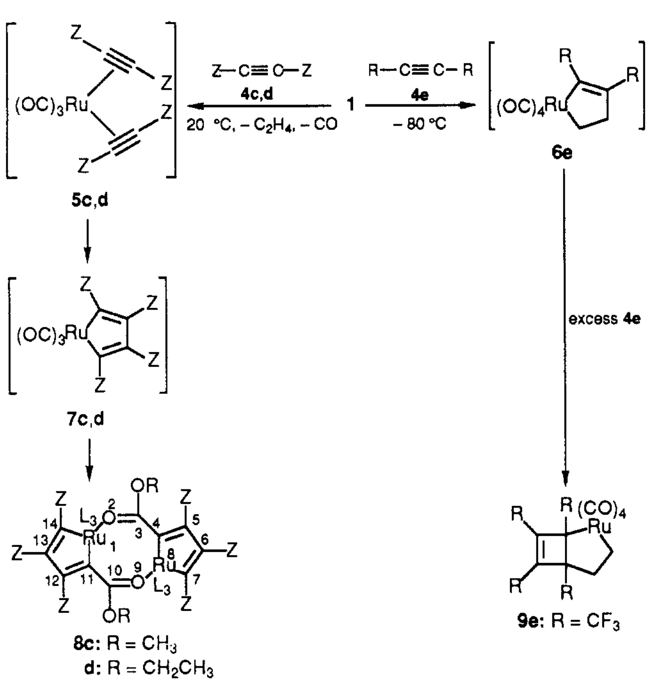
Scheme II



L = CO; Z = CO_2R

the formation of the tricyclic systems **8c,d** (Scheme II). In a first step ethene and one carbon monoxide ligand are each substituted by a molecule of **4c,d** to give the bis(alkyne) complexes **5c,d**. Subsequently a C–C bond is formed yielding the ruthenacyclopentadienes **7c,d**. **5c,d** and **7c,d** have been not detected. The unstable 16-electron fragments **7c,d** are stabilized immediately by dimerization. An ester carbonyl function next to ruthenium in **7c,d** coordinates to the ruthenium atom of a second metallacyclopentadiene unit and vice versa.

The weak donor bonds in **8c,d** play a key role in understanding the reactivity of these heterocycles. This type of compound is a catalyst for the cyclotrimerization of acetylenedicarboxylic acid dialkyl esters **4c,d** to give the corresponding benzenehexacarboxylic acid hexaalkyl esters **13c,d**. The turnover numbers are on the order of 200 h^{-1} (experiments are not optimized). Corresponding to the research work of other groups on the cyclotrimerization of alkynes[15] we suggest a catalytic cycle as shown in Scheme III. The inital step in the catalytic process is the cleavage of the weak O–Ru donor bonds in **8c,d** in the presence of additional alkynes. After insertion of an alkyne molecule in one of the Ru–C bonds of the intermediates **11c,d** 16-electron unsaturated seven-membered metallacycles **12c,d** are to be expected. Reductive elimination of the organic ring fragment from **12c,d** yields the benzenehexacarboxylic acid hexaalkyl esters **13c,d** as the products of this catalysis. Via the 16-electron (η^2-alkyne)$Ru(CO)_3$ complexes **14c,d** and the metallacyclopentadienes **15c,d** the starting compounds **11c,d** are re-formed.

At 40 °C **8c,d** react in solutions of acetone with CO (5 bar) yielding the hitherto unknown metallacyclopentadienes **10c,d** (Scheme III). The compounds were characterized by their IR, mass, and ^1H and $^{13}C\{^1H\}$ NMR

Scheme III

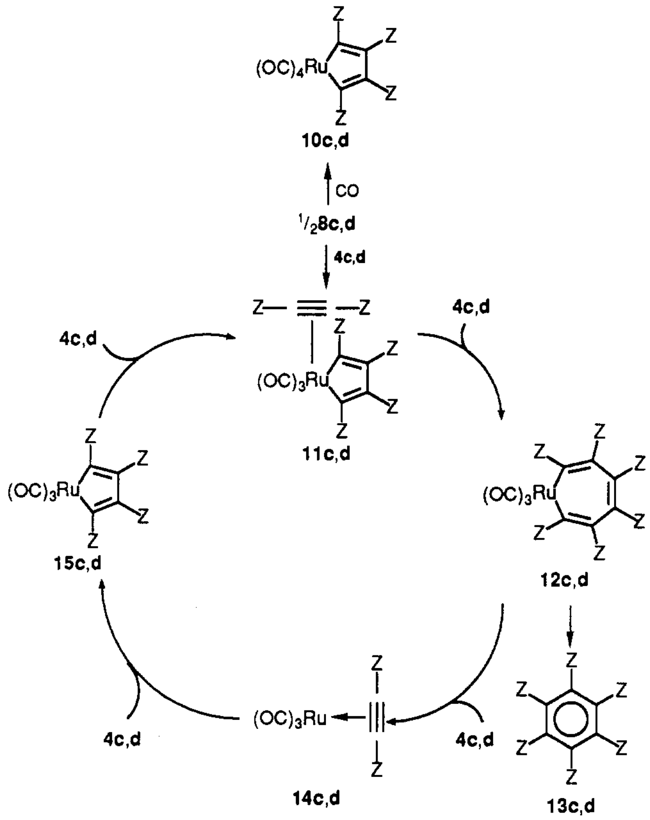


Table II. Selected Interatomic Distances (Å) and Angles (deg) for 8d

Bond Lengths			
Ru-O(4)	2.118 (2)	C(3)-O(3)	1.115 (5)
Ru-C(1)	1.976 (4)	C(4)-C(5)	1.347 (5)
Ru-C(2)	1.978 (4)	C(5)-C(6)	1.471 (5)
Ru-C(3)	1.876 (5)	C(6)-C(7)	1.352 (5)
Ru-C(4)	2.118 (3)	C(8)-O(4)	1.243 (5)
Ru-C(7)	2.109 (3)	C(8)-O(5)	1.315 (5)
C(1)-O(1)	1.123 (4)	C(4)-C(8′)	1.452 (5)
C(2)-O(2)	1.121 (5)		

Bond Angles			
O(4)-Ru-C(1)	85.3 (1)	Ru-O(4)-C(8)	115.5 (4)
O(4)-Ru-C(2)	98.7 (1)	Ru-C(1)-O(1)	116.3 (3)
O(4)-Ru-C(3)	172.6 (1)	Ru-C(2)-O(4)	115.4 (2)
O(4)-Ru-C(4)	91.0 (1)	Ru-C(3)-O(4)	119.1 (2)
O(4)-Ru-C(7)	82.3 (1)	Ru-C(4)-C(5)	115.0 (2)
C(1)-Ru-C(2)	94.8 (2)	Ru-C(4)-C(8′)	176.3 (5)
C(1)-Ru-C(3)	95.4 (2)	Ru-C(7)-C(6)	171.8 (3)
C(1)-Ru-C(4)	170.3 (1)	C(4)-C(5)-C(6)	175.9 (3)
C(4)-Ru-C(7)	77.7 (1)	C(5)-C(6)-C(7)	132.5 (2)

spectra. In the region of terminal CO groups in the IR spectra of **10c,d** appear four bands with the typical patterns for $M(CO)_4$ fragments. Due to their ring conformation the $^{13}C\{^1H\}$ NMR spectra of **10c,d** each show two signals for the terminal carbon monoxide ligands and the ester carbonyl functions.

Description of the Crystal Structure of 8d. The crystal structure of **8d** is built up of discrete dinuclear molecules (Figure 1). Table II contains selected bond distances and angles. Final atomic positional parameters for **8d** are listed in Table III. The geometry surrounding each ruthenium atom is roughly octahedral, and the dimeric structure is realized by the Ru–O(4) bond, the O(4) atom belonging to one of the ester groups attached to the opposite metallacyclopentadiene system. The eight-membered ring has a chair conformation with a crystallographic center of inversion. The atoms of the metallacyclo-

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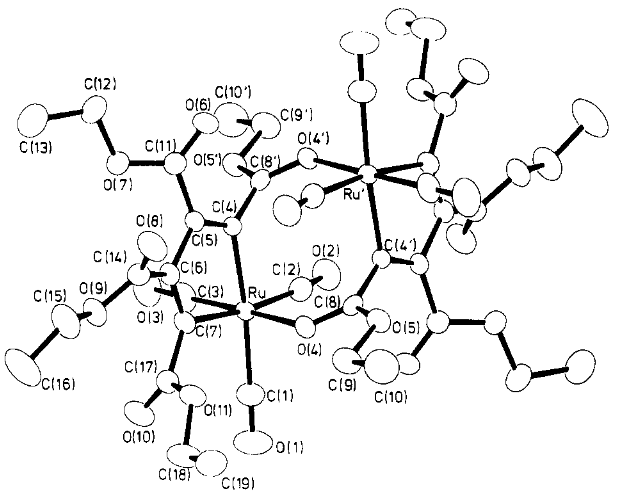

Figure 1. ORTEP plot of **8d**.

Table III. Fractional Atomic Coordinates (Esd's in Parentheses) of 8d with Equivalent Isotropic Thermal Parameters U_{eq} (Å^2)^a

atom	x	y	z	U_{eq}
Ru	0.47005 (3)	0.09958 (2)	0.14999 (4)	0.022 (2)
O(1)	0.4366 (4)	0.2712 (2)	0.1117 (6)	0.066 (4)
O(2)	0.7045 (3)	0.0996 (3)	0.1349 (4)	0.043 (2)
O(3)	0.5195 (3)	0.1009 (3)	0.4637 (4)	0.061 (3)
O(4)	0.4126 (2)	0.0937 (2)	−0.0663 (3)	0.026 (2)
O(5)	0.3881 (3)	0.0630 (2)	−0.2917 (4)	0.031 (2)
O(6)	0.3948 (3)	−0.1788 (2)	0.1685 (4)	0.043 (2)
O(7)	0.2877 (3)	−0.1350 (2)	0.3191 (4)	0.049 (2)
O(8)	0.1430 (3)	−0.0662 (2)	0.1028 (4)	0.042 (2)
O(9)	0.1175 (3)	0.0308 (2)	0.2450 (4)	0.035 (2)
O(10)	0.2427 (3)	0.1988 (2)	0.2465 (4)	0.042 (2)
O(11)	0.1810 (3)	0.1454 (2)	0.0412 (4)	0.035 (2)
C(1)	0.4524 (4)	0.2095 (3)	0.1275 (6)	0.033 (3)
C(2)	0.6186 (4)	0.1007 (3)	0.1297 (5)	0.032 (3)
C(3)	0.5033 (4)	0.1023 (3)	0.3465 (6)	0.036 (3)
C(4)	0.4612 (3)	−0.0189 (3)	0.1689 (5)	0.022 (2)
C(5)	0.3675 (4)	−0.0457 (3)	0.1874 (5)	0.024 (2)
C(6)	0.2847 (4)	0.0103 (3)	0.1868 (5)	0.026 (3)
C(7)	0.3139 (4)	0.0829 (3)	0.1764 (5)	0.028 (3)
C(8)	0.4457 (4)	0.0634 (3)	−0.1696 (5)	0.024 (2)
C(9)	0.2845 (4)	0.0951 (4)	−0.2946 (6)	0.039 (3)
C(10)	0.2302 (5)	0.0806 (4)	−0.4392 (7)	0.057 (5)
C(11)	0.3518 (4)	−0.1274 (3)	0.2195 (5)	0.028 (3)
C(12)	0.2677 (5)	−0.2118 (3)	0.3609 (7)	0.046 (3)
C(13)	0.1825 (5)	−0.2091 (4)	0.4534 (8)	0.068 (5)
C(14)	0.1758 (4)	−0.0141 (3)	0.1732 (6)	0.028 (3)
C(15)	0.0075 (4)	0.0178 (4)	0.2260 (7)	0.047 (4)
C(16)	−0.0404 (5)	0.0764 (4)	0.3057 (9)	0.070 (5)
C(17)	0.2419 (4)	0.1478 (3)	0.1639 (6)	0.030 (3)
C(18)	0.1156 (5)	0.2115 (3)	0.0111 (7)	0.050 (4)
C(19)	0.0496 (5)	0.1973 (4)	−0.1226 (7)	0.048 (4)

^{a} $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$.

pentadiene ring lie in one plane (within 0.02 Å). The bond sequence long–short–long for C(4)–C(5), C(5)–C(6), and C(6)–C(7) is typical for a cyclopentadiene ring.[16] The value of the Ru–O(4) bond length agrees with those reported in the literature.[17] Because a lone pair of electrons of the O(4) atom is involved in the ligand–metal σ-bond, the C(8)–O(4) distance is significantly longer than those for the other noncoordinated ester CO groups. Due to the trans effect, the Ru–C(3) bond is 0.1 Å shorter than the two carbonyl groups with CO(av) = 1.97 Å.

Behavior of 1 toward Hexafluoro-2-butyne (4e). Surprisingly, in the presence of hexafluoro-2-butyne (**4e**) **1** reacts in quite another way. If **4e** is condensed into a −80 °C cold ethene-saturated solution of **1** in *n*-pentane and subsequently the solution is allowed to warm to room temperature under an atmosphere of **4e**, the colorless ruthenabicyclo[3.2.0]heptene **9e** is isolated in good yield (Scheme II). In contrast to the behavior of the ruthenium complex **1** toward the alkenes **3a,b**, with **4e** it reacts like a metallacyclopropane.[18] It is known that metallacyclopropanes with group IVb metals undergo insertion reactions with alkynes to give ring-expanded heterocycles.[19] In conformity with this observation the alkyne **4e** is inserted into a Ru–C bond of **1** with formation of the proposed intermediate **6e**. A second molecule of hexafluoro-2-butyne (**4e**) reacts in a [2 + 2] cycloaddition with the double bond of **6e**. The different conditions between the reaction of **1** with **4c,d** (20 °C) and with **4e** (−80 °C) would appear to explain the unexpected product **9e**. At −80 °C the olefin in **1** is not substituted in the presence of **4e** because the ruthenium–ethene bond is too strong under these conditions.

The $(OC)_4Ru$ fragment of **9e** gives rise to four sharp CO absorptions in the IR spectrum (*n*-hexane). Due to the electron-withdrawing effect of the CF_3 groups the C≡O stretching frequencies are markedly shifted to higher wavenumbers. The band at 1653 cm^{-1} is assigned to ν-(C=C).

In the 400-MHz ^{1}H NMR spectrum of **9e** four multiplets are observed for the methylene protons. Simulation of the spectrum shows an $ABCDX_3$ spin system. We assign the two multiplets, which correspond to fluorine–hydrogen coupling, to the β-methylene groups. The difference in their chemical shifts may be traced back to an interaction of the protons with the CO ligands or the C=C double bonds in **9e**.

In the $^{13}C\{^1H\}$ NMR spectrum of **9e** three signals occur for the CO ligands, four quartets for the CF_3 groups, and two signals for the methylene C atoms. Because of the coupling of the β-methylene carbon atom with the fluorine atoms of the CF_3 groups, this peak has a multiplet structure. The signal at δ 186.38 is assigned to the CO group which is trans to C(2). Because the absorption at δ 185.05 shows no fluorine–carbon coupling, we assign it to the CO group which is trans to C(6). For the carbon atoms directly bound to the CF_3 groups four multiplets are observed. The two high-field absorptions are assigned to the sp^3-hybridized C atoms (δ 30.08, 22.68); the two downfield absorptions are traced back to the sp^2-hybridized C atoms (δ 140.13, 136.99) of the four-membered ring fragment (Scheme II). In addition **9e** was characterized by its mass spectrum, a molecular weight determination, and elemental analysis.

Conclusion

The above results are an example of a wide variety of reactions of a tetracarbonyl(η^2-ethene)metal complex of the iron group. We have shown that the products depend on both the type of ligand and the reaction conditions. **1** offers a simple route to the tricyclic systems **8c,d**. The unusual coordination of two ester carbonyl functions to the ruthenium atoms in **8c,d** represents an interesting chemistry of these compounds, which are good catalysts for the cyclotrimerization of acetylenedicarboxylic acid dialkyl esters. The facile cleavage of the weak Ru–O donor

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bond suggests **8c,d** as a source of new, hitherto unknown products.

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Registry No. 1, 52621-15-5; **2a**, 17656-09-6; **2b**, 670-54-2; **3a**, 122145-45-3; **3b**, 122145-46-4; **4c**, 762-42-5; **4d**, 762-21-0; **4e**, 692-50-2; **8c**, 122145-47-5; **8d**, 122145-48-6; **9e**, 122171-17-9; **10c**, 122145-49-7; **10d**, 122145-50-0; **13c**, 6237-59-8; **13d**, 91620-99-4.

Supplementary Material Available: Tables of least-squares planes, final positional and anisotropic parameters, and interatomic distances and angles for **8d** (7 pages); a listing of observed and calculated structure factors for **8d** (21 pages). Ordering information is given on any current masthead page.

Stereoselective Syntheses of Coordinated Secondary and Tertiary Phosphines. Crystal and Molecular Structure of $[(R^*,R^*),(R^*)]$-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PHMePh)]PF_6\cdot 0.5CH_2Cl_2$

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Reaction of (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PH_2Ph)]PF_6$ with methyl or ethyl iodide in the presence of triethylamine at 20 °C produces separable mixtures of the corresponding alkyl derivatives $[(R^*,R^*),(R^*)]$-(±)- and $[(R^*,R^*),(S^*)]$-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PHRPh)]PF_6$ (R = Me or Et) with ca. 3.5:1 diastereoselectivity in favor of the $[(R^*,R^*),(R^*)]$ diastereomer in each case. Major diastereomer $[(R^*,R^*),(R^*)]$-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PHMePh)]PF_6\cdot 0.5CH_2Cl_2$ crystallizes in the monoclinic space group $P2_1/n$ (nonstandard No. 14) with a = 11.013 (9) Å, b = 26.143 (14) Å, c = 11.551 (4) Å, β = 90.65 (5)°, V = 3325.5 Å^3, d_{calcd} = 1.51 g cm^{-3}, Z = 4, and R = 0.051 (R_w = 0.046) for 2768 data having $[I > 3\sigma(I)]$. The secondary phosphido–iron complex (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}FePHPh]\cdot$thf was isolated by deprotonation of the primary phosphine compound with KOBu-*t* in tetrahydrofuran; variable-temperature ^{1}H NMR spectra of this complex in $[^2H_8]$tetrahydrofuran gave $\Delta G^{\ddagger}$ (253 K) = 60 ± 4 kJ mol^{-1} for the inversion barrier of the pyramidal phenylphosphido–iron phosphorus stereocenter in the molecule with the diastereomer ratio $[(R^*,R^*),(R^*)]$:$[(R^*,R^*),(S^*)]$ = 4.5:1 at the slow-exchange limit (−65 °C). Alkylations of the secondary phenylphosphido–iron intermediate at −65 °C give secondary phosphine complexes with diastereoselectivities corresponding to the concentrations of secondary phosphido–iron diastereomers at equilibrium (4.5:1). At −95 °C, however, deprotonation of the secondary phosphine complex $[(R^*,R^*),(R^*)]$-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PHMePh)]PF_6\cdot 0.5CH_2Cl_2$ is stereospecific giving the tertiary phosphido–iron complex $[(R^*,R^*),(R^*)]$-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}FePMePh]$ with complete stereoselectivity, as demonstrated by the quantitative recovery of the diastereomerically pure starting material following acidification of the reaction mixture at this temperature. Alkylations of the tertiary phosphido–iron complex, generated and maintained at −95 °C, also proceed with retention of configuration and complete stereoselectivity; reactions above this temperature give mixtures of thermodynamic products because of the relatively low barrier to inversion of the pyramidal phosphorus stereocenter in the intermediate tertiary phosphido–iron complex ($\Delta G^{\ddagger}$ (278 K) = 59 ± 2 kJ mol^{-1}). The corresponding optically active complexes of (±)-methylphenylphosphine have also been prepared, the first examples of complexes containing resolved secondary phosphines.

Introduction

Primary and secondary phosphine–metal complexes[1,2] are readily deprotonated giving terminal phosphido–metal complexes.[2-6] Depending upon substituents, the terminal phosphido–metal groups in the complexes are pyramidal and nucleophilic (M—PX$_2$) or planar and electrophilic (M$^-$=P$^+$X$_2$).[4-6] For example, pyramidal phosphido–metal complexes react with metal ions to give bridging phosphido–metal complexes[3,7] and with alkyl halides to give substituted phosphine–metal complexes.[6] Secondary

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