Preparation, Properties, and Reactions of Metal-Containing Heterocycles, XC[1]

Reactivity of Differently Activated Alkynes toward Ruthenium and Osmium Complexes of the Type $(\eta^2\text{-}C_2H_4)M(CO)_4$☆

Ekkehard Lindner*, Hartwig Kühbauch, and Hermann A. Mayer

Institut für Anorganische Chemie der Universität Tübingen,
Auf der Morgenstelle 18, D-72076 Tübingen, Germany

Received January 10, 1994

Key Words: Ruthenium compounds / Osmium compounds / Alkynes, activated / Cyclotrimerization

Depending on the substituents, the reaction of the activated alkynes ZC≡CZ (**2a–g**) [Z = CO_2R: R = Me (**a**), Et (**b**); Z = R^1: R^1 = CF_3 (**c**), CH_2Cl (**d**), CH_2Br (**e**); Z = $CH_2OC(O)R^2$: R^2 = Me (**f**), CCl_3 (**g**)] with the labile ruthenium complex $(\eta^2\text{-}C_2H_4)Ru(CO)_4$ (**1**) results in the formation of three different types of heterocycles. While the reactions of the dialkyl acetylenedicarboxylates **2a**, **b** lead to the dimeric tricarbonylruthenacyclopentadienes **3a**, **b**, being catalytically active in the cyclotrimerization of alkynes like **2a**, **b**, the application of the 1,4-halogeno-2-butynes **2c–e** yields the bicyclic heterocycles **4c–e**. The esters of 2-butyne-1,4-diol **2f**, **g** are converted into the tetracarbonylruthenacyclopentadienes **5f**, **g**. Investigation of the primary attack of the alkynes **2a–g** at complex **1** leads to the conclusion, that an ionic mechanism is preferred in the ruthenium-catalyzed cyclotrimerization of electron-poor alkynes. If, instead of **1**, $(\eta^2\text{-}C_2H_4)Os(CO)_4$ (**6**) is allowed to react with the acetylenes **2a**, **b** the osmium complexes $(\eta^4\text{-}C_6Z_6)Os(CO)_3$ (**7a**, **b**) are isolated. In the presence of CO at 2 bar **7a**, **b** release the benzene derivatives C_6Z_6 (**8a**, **b**) with the formation of $Os_3(CO)_{12}$.

The reactivity of alkynes toward transition-metal complexes has been extensively investigated during the last two decades[2–5]. In most cases a cyclooligomerization takes place at the metal center resulting in a great variety of heterocycles[6]. While nickel[7] and cobalt[8] are already classical catalysts used in cyclooligomerizations of differently substituted acetylenes, complexes of the iron triad show a significantly lower tendency toward catalytic activity. Due to the easy formation of cluster structures many of these compounds possess at least two metal centers[9,10]. Mechanistic aspects of the cyclotrimerization of alkynes have been preferably examined with cobalt[4], rhodium[5], and palladium[11], showing that metallacyclopentadienes are important intermediates in those reaction pathways.

Depending on the oxidation state of the employed transition metals and the kind of the acetylenes, two different mechanisms are discussed in the literature. An ionic mechanism[11,12] is preferred if alkynes with electron-withdrawing substituents and electron-rich metals are used. The bis(η^2-alkyne) complex type is favored if the transition metal has a higher oxidation state and the alkyne is less electron-deficient[11].

Recently, a dimeric ruthenacyclopentadiene with catalytic activity toward the cyclotrimerization of dimethyl acetylenedicarboxylate (DMAD) has been obtained by our research group[13,14]. The catalytic cycle of that reaction is not yet clear in detail. Therefore, in the present paper we have focused in particular on the elements ruthenium and osmium to investigate which of the above-mentioned mechanisms is relevant for this specific reaction. For this reason the behavior of the labile $(\eta^2\text{-}C_2H_4)M(CO)_4$ complexes toward different activated alkynes is studied.

Results and Discussion

The reaction of $(\eta^2\text{-}C_2H_4)Ru(CO)_4$ (**1**) with the dialkyl acetylenedicarboxylates **2a**, **b** in *n*-hexane solution results in the formation of the surprisingly stable intermediates **3a**, **b**[13]. These molecules consist of two ruthenacyclopentadiene units which are connected by coordination of the metal-adjacent ester carbonyl oxygen functions to ruthenium leading to a tricyclic system. With excess alkyne at elevated temperatures a catalytic cyclotrimerization takes place yielding the corresponding esters of benzenehexacarboxylic acid.

The stable coordination of the ester carbonyls in **3a**, **b** leads to the supposition that this group could possibly play an important role in the primary attack of the alkyne. To support this suggestion, the behavior of activated alkynes of the 1,4-halogeno-2-butyne type **2c–e** without ester carbonyl groups toward complex **1** has been studied. However, this reaction proceeds in a completely different way and the kind of the products **4c**[13], **d**, **e**, which are not catalytically active, is in contrast to that of **3a**, **b**. Compounds **4c–e** are obtained in good yields after recrystallization from acetone/*n*-hexane as colorless to pale yellow complexes, which are soluble in most polar organic solvents, sensitive to air and temperature in solution, but fairly stable in the solid state.

First, the corresponding alkyne is inserted into one of the ruthenium-carbon bonds of the $(\eta^2\text{-}C_2H_4)Ru$ moiety to give an unstable ruthenacyclopentene which immediately un-

  0009–2940/94/0808–1343 $ 10.00+.25/0

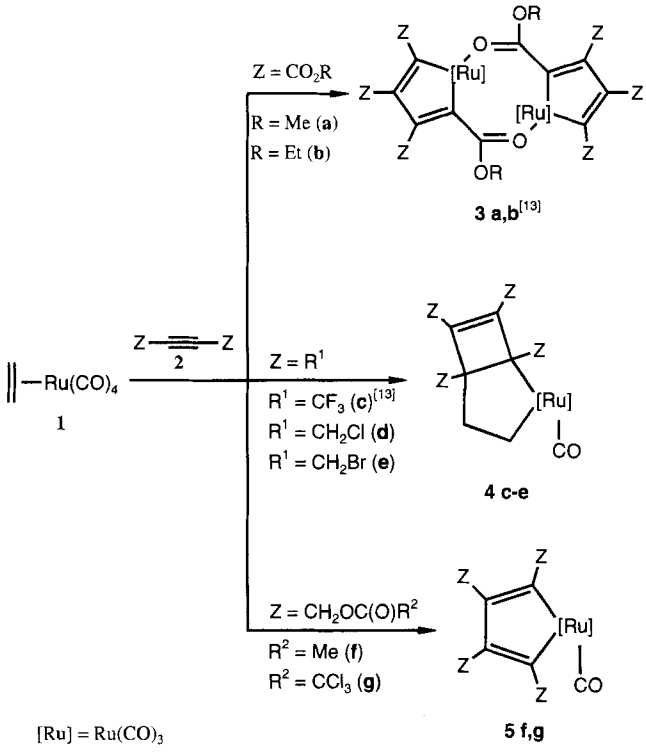
dergoes a [2+2] cycloaddition with a second alkyne molecule to form the bicyclic systems **4c–e**. While the composition of **4d** has been confirmed by a field-desorption mass spectrum, showing the molecular peak, in the case of **4e** an osmometric molecular mass determination has been carried out. In the IR spectra **4d, e** are characterized by four intensive CO absorptions in the 5-μm range. The $^{13}C\{^1H\}$-NMR spectra of **4d, e** are comparable with each other, and the signal pattern can be separated into five signal groups. Two high-field resonances are typical of the metal-adjacent carbon atoms. Next to these signals are two further singlets in the downfield region which are ascribed to the quaternary carbon atoms in the ruthenacyclopentane part of the bicyclic ring system. Another peak in the middle range is assigned to the olefinic carbon atoms which do not give rise to individual signals. At lowest field only two peaks due to the four CO ligands are observed. Thus, **4d, e** have the same structure as the already published complex **4c**[13] and are depicted in Scheme 1.

The significant difference in the behavior of the ruthenium complex **1** toward the alkynes **2a, b** and **2c–e** has prompted us to carry out additional experiments regarding the primary attack of the alkynes at the complex **1**. Whereas with **2a, b** a displacement of ethylene and a CO ligand prevails, in the reaction with **2c–e** both ligands are not exchanged. These observations do not agree with the consecutive formation of an $(\eta^2\text{-alkyne})_2Ru$ complex, as it happens in the cobalt-catalyzed cyclotrimerization of alkynes[4]. To verify this hypothesis another type of alkynes has been employed. The carbonyl function of the alkyl esters of 2-butyne-1,4-diol **2f, g** are in another position as in **2a,b** so that these ligands are not able to form eight-membered rings by dimerization as observed in the case of **3a, b**.

In contrast to the alkynes **2a, b**, in *n*-hexane **2f, g** expel only the ethylene molecule in the starting complex **1**. No release of a CO ligand occurs even under a vigorous bubbling flow of ethylene during the reaction. If argon instead of ethylene is applied rapid decomposition of complex **1** takes place resulting in the formation of $Ru_3(CO)_{12}$. The pale yellow tetracarbonylruthenacyclopentadienes **5f, g** are surprisingly stable to air, even in solution, and dissolve readily in polar organic solvents. Even at higher temperatures no catalytic activity toward excess alkyne has been found. In the field-desorption and ion-spray mass spectra the complexes **5f, g** exhibit the expected molecular peak and the M − 3 CO peak, respectively. Four intensive CO bands in the 5-μm region of the IR spectra of **5f, g** are assigned to the *cis*-$Ru(CO)_4$ fragments. Between 1770 and 1720 cm^{-1} a sharp absorption appears which is characteristic of the ester carbonyl functions.

Whereas in the ^1H-NMR spectrum of **5f** two multiplets between δ = 5.0 and 4.7 are attributed to the protons of the four methylene groups, of which the α- and β-positioned species are equivalent, in the corresponding spectrum of **5g** only one unresolved multiplet is observed. A singlet at δ = 2 can be assigned to the protons of the four methyl groups of **5f**.

Scheme 1

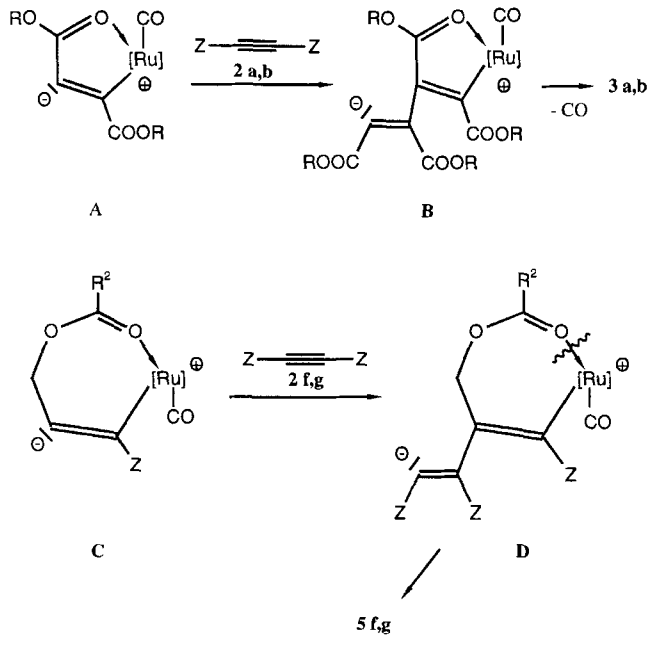


Both $^{13}C\{^1H\}$-NMR spectra of **5f, g** show six separated signals. At lowest field the two peaks are typical of the $Ru(CO)_4$ moiety which are followed by a multiplet for the ester carbonyl carbon atoms. Next to these resonances two singlets can be assigned to the α and β ring carbon atoms, respectively. As expected, the ruthenium-adjacent carbon atoms remarkably absorb at lower frequency. At highest field the signals for the methylene, methyl, and trichloromethyl carbon atoms are observed.

The above-mentioned experiments have demonstrated that an ester carbonyl function is necessary to displace the ethylene ligand in complex **1**, as is the case with the alkynes **2a, b, f, g**. If an ionic mechanism[11,12] as depicted in Scheme 2 is assumed, the cleavage of the metal-carbon bond of a CO ligand in the reaction with **2a, b** may be rationalized by the formation of a five-membered intermediate **A**, with ruthenium in the formal oxidation state +II[11]. The attack of the second alkyne molecule (**A** → **B**), which is necessary for the formation of a ruthenacyclopentadiene ring, is only possible, if a CO ligand is displaced. To eliminate carbon monoxide in the reaction between **1** and the alkynes **2f, g** a seven-membered ring **C** should be formed which, in contrast to a five-membered ring, is energetically not favored. Thus, without CO elimination, an empty coordination site is available which is occupied by the second alkyne (**C** → **D** → **5f, g**) to form the ruthenacyclopentadiene rings **5f, g**.

These results are in accordance with the hitherto vain efforts to synthesize a complex of the type $(\eta^2\text{-DMAD})Ru(CO)_4$. In the light of these facts the postulated mechanism for the ruthenium-catalyzed cyclotrimerization of di-

Scheme 2

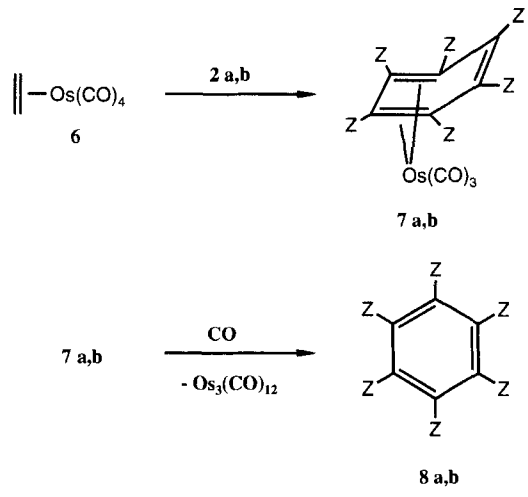


alkyl acetylenedicarboxylates[13] has to be changed to the ionic form.

To get a more profound insight into the reaction pathway of the above-mentioned cyclization of activated alkynes we have used osmium instead of ruthenium for two reasons: the tricyclic compounds **3a, b** as starting complexes are too stable to react with such alkynes under moderate conditions. If higher temperatures are employed the cyclotrimerization products **8a, b** are immediately formed without the opportunity to detect further intermediates[13]. To elude this problem the same reaction was carried out with **2a, b** and the osmium complex **6** in *n*-hexane (Scheme 3). In comparison with ruthenium, the stability of osmium-(acetylene)carbon bonds is much higher. As exclusive products the colorless, air-stable, in polar organic solvents soluble compounds **7a, b** have been isolated, independent on the alkyne to osmium ratio which was varied from 1:1 to 4:1. In the field-desorption mass spectra of **7a, b** the molecular peaks are observed, and the IR spectra show three intensive bands in the 5-μm region which are attributed to the $Os(CO)_3$ group in each case.

The signals in the $^{13}C\{^1H\}$-NMR spectra of **7a, b** are located in four distinct areas. The two downfield resonances can be assigned to the carbon atoms of the $Os(CO)_3$ fragment, followed by three singlets for the ester carbonyl carbon atoms at higher field. Three clearly separated signals occur in the olefinic range and are characteristic of an η^4-coordinated benzene derivative[18]. At lowest frequencies the peaks for the carbon atoms of the methyl and ethyl groups appear. Interestingly, up to 30°C no fluxional behavior of the cyclotrimeric fragment in **7a, b** is observed as described in the literature for similar complexes[18]. Heating of [D_6]acetone solutions of **7a, b** to higher temperatures results in a decomposition of these compounds. Due to the strong downfield shift of the ring carbon atoms a metallanorbornadiene species, which can also be discussed as the final intermediate in the cyclotrimerization of alkynes, is unequivocally excluded[4]. Also no dimeric form in analogy to **3a, b** occurs, which leads to the conclusion that the intermediate (monomeric) tricarbonylosmacyclopentadiene reacts much faster with another alkyne molecule than with a second monomer. In contrast to the analogous ruthenium compounds[14], higher substituted alkynes such as the di-*n*-propyl acetylenedicarboxylate do not react with the osmium complex **6**.

Scheme 3



Treatment of solutions of **7a, b** in ethyl methyl ketone with carbon monoxide for one hour in a pressure Schlenk tube at 2 bar and 50°C leads to cleavage of the coordinated cyclotrimers **8a, b** with the formation of the $Os_3(CO)_{12}$ cluster. In the case of **7a** even moderate heating to 40°C in ethyl methyl ketone solution, without pressurizing with CO, may cause elimination of the benzene derivative **8a**, supporting the presumption that **7a, b** are intermediates in the catalytic cyclotrimerization of activated alkynes.

Conclusion

Reaction of the ruthenium complex **1** with the differently activated alkynes **2a–g** leads to three product types indicating a different reaction pathway, depending on the substituents of the employed acetylenes. Experiments regarding the primary attack of the alkyne at the starting complex **1** lead to an improved understanding of the first steps in the ruthenium-catalyzed cyclization of activated alkynes.

Because of its more stable metal-carbon bonds osmium complexes are commonly used as model compounds for reactive intermediates in catalytic cycles[20]. Therefore, the osmium complex **6**, in analogy to **1**, has been employed to synthesize the fairly stable compounds **7a, b**. Corresponding species have not been obtained in the comparable ruthenium chemistry.

H. K. acknowledges the *Land Baden-Württemberg* for the award of a Ph. D. Fellowship. Support of this work by *Verband der Chemischen Industrie e. V.*, *Fonds der Chemischen Industrie* is gratefully

acknowledged. Thanks are also due to the *BASF Aktiengesellschaft* and the *Degussa AG* for providing valuable starting materials.

Experimental

All reactions were carried out under oxygen-free and dried argon. The solvents were dried according to common procedures and were saturated with argon. Synthesis of the starting compounds **1** and **6** is described in refs.[15-17]. Alkynes **2a**, **b**, **d**–**g** were synthesized by using common procedures.

MS (FD): Finnigan MAT 711A modified by AMD (8 kV, 60°C). – MS (Ion Spray): Perkin-Elmer SCIEX API III. – IR: Bruker IFS 48. – ^{1}H NMR: Bruker AMX 400, AC 250 and Bruker AC 80 at 400.14, 250.13, and 80.13 MHz. – ^{13}C{^{1}H} NMR: Bruker AMX 400, Bruker AC 250, and Bruker AC 80 at 100.61, 62.90, and 20.15 MHz. Chemical shifts were measured relative to partially deuterated solvent peaks which are reported relative to tetramethylsilane. Measurement temp. 295 K. – Microanalyses: Carlo Erba, model 1106 and AAS Perkin-Elmer, model 4000. – Osmometric molecular mass determination: Knauer Dampfdruckosmometer, standard: benzil. – Elemental analyses of ruthenium were carried out as reported in ref.[19].

General Procedure for the Synthesis of the Heterocycles **4d**, **e**: To a cooled ethylene-saturated solution of **1** in *n*-hexane (−10°C) stoichiometric amounts of **2d**, **e** were added. Stirring for 30 min at this temp. completed the reaction (IR control), and a pale yellow precipitate was formed. Filtration (P3), drying in vacuo, and recrystallization from *n*-hexane/acetone yielded the pure products **4d**, **e** which readily dissolved in polar organic solvents. The dried complexes were fairly air-stable. They rapidly decomposed upon exposure to air.

1) *2,2,2,2-Tetracarbonyl-1,5,6,7-tetrakis(chloromethyl)-2-ruthenabicyclo[3.2.0]hept-6-ene* (**4d**): A solution of **1** (226 mg, 0.93 mmol) in 80 ml of *n*-hexane was allowed to react with **2d** (235 mg, 1.91 mmol) to give 132 mg (29%) of pure **4d**, m.p. 73°C (dec.). – Mol. mass: 488 (osmometric, solvent: benzene). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2130, 2056, 2019, 2002 cm^{-1} (C≡O). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.65 (m, 2H, $RuCH_2$), 1.14 (m, 2H, $RuCH_2CH_2$), 3.83, 3.95 (m, 8H, CH_2Cl). – ^{13}C{^{1}H} NMR (63 MHz, [D$_6$]acetone): δ = 187.05, 184.02 (s, C≡O), 122.37 (s, $=CCH_2Cl$), 33.06, 31.28 (s, CH_2Cl), 28.54 (s, $RuCCH_2Cl$), 22.30 (s, CH_2CCH_2Cl), 20.72 (s, $RuCH_2CH_2$), 9.05 (s, $RuCH_2$). – $C_{14}H_{12}Cl_4O_4Ru$ (487.1): calcd. C 34.52, H 2.48, Cl 29.11, Ru 20.75; found C 33.95, H 3.03, Cl 29.29, Ru 21.78.

2) *1,5,6,7-Tetrakis(bromomethyl)-2,2,2,2-tetracarbonyl-2-ruthenabicyclo[3.2.0]hept-6-ene* (**4e**): A solution of **1** (200 mg, 0.84 mmol) in 150 ml of *n*-hexane was allowed to react with **2e** (396 mg, 1.87 mmol) to give 178 mg (32%) of pure **4e**, m.p. 84°C (dec.). – MS (FD), *m/z*: 662 [M$^+$, rel. to ^{79}Br and ^{102}Ru]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2134, 2069, 2015, 1990 cm^{-1} (C≡O). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.54 (m, 2H, $RuCH_2$), 1.15 (m, 2H, $RuCH_2CH_2$), 3.33, 3.47 (m, 8H, CH_2Br). – ^{13}C{^{1}H} NMR (63 MHz, [D$_6$]acetone): δ = 186.87, 183.59 (s, C≡O), 114.44 (s, $=CCH_2Br$), 38.40, 31.00 (s, CH_2Br), 27.02 (s, $RuCCH_2Br$), 22.44 (s, CH_2CCH_2Br), 20.16 (s, $RuCH_2CH_2$), 8.82 (s, $RuCH_2$). – $C_{14}H_{12}Br_4O_4Ru$ (664.9): calcd. C 25.29, H 1.82, Br 48.07, Ru 15.20; found C 25.42, H 1.83, Br 46.95, Ru 15.85.

General Procedure for the Synthesis of the Heterocycles **5f**, **g**: To a cooled ethylene-saturated solution of **1** in *n*-hexane (−10°C) stoichiometric amounts of **2f**, **g** were added. Warming to room temp. and stirring for 60 min at this temp. completed the reaction (IR control). Cooling to −30°C yielded a pale yellow precipitate. Filtration (P3), drying in vacuo, and recrystallization from *n*-hexane/acetone yielded the pure air-stable products **5f**, **g** which readily dissolved in polar organic solvents.

3) *2,3,4,5-Tetrakis(acetoxymethyl)-1,1,1,1-tetracarbonyl-ruthenacyclopentadiene* (**5f**): A solution of **1** (203 mg, 0.84 mmol) in 100 ml of *n*-hexane was allowed to react with **2f** (324 mg, 1.90 mmol) to give 200 mg (43%) of pure **5f**, m.p. 114°C (dec.). – MS (FD), *m/z*: 554 [M$^+$, rel. to ^{102}Ru]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2097, 2043, 2024, 1973 cm^{-1} (C≡O), 1741 (C=O). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 5.0–4.9 (m, 4H, CH_2), 4.8–4.7 (m, 4H, CH_2), 2.02 (s, 12H, CH_3). – ^{13}C{^{1}H} NMR (20 MHz, $CDCl_3$): δ = 192.20, 173.30 (s, C≡O), 169.92 (m, C=O), 100.29 (s, $RuC=CCH_2$), 75.91 (s, RuC=), 56.27, 55.40 (s, CH_2), 20.37 (s, CH_3). – $C_{20}H_{20}O_{12}Ru$ (553.5): calcd. C 43.41, H 3.64, Ru 18.26; found C 43.52, H 3.70, Ru 18.75.

4) *1,1,1,1-Tetracarbonyl-2,3,4,5-tetrakis(trichloroacetoxymethyl)-ruthenacyclopentadiene* (**5g**): A solution of **1** (282 mg, 1.17 mmol) in 80 ml of *n*-hexane was allowed to react with **2g** (900 mg, 2.39 mmol) to give 825 mg (73%) of pure **5g**, m.p. 102°C (dec.). – MS (IS), *m/z*: 880 [M$^+$ − 3 CO, rel. to ^{35}Cl and ^{102}Ru]. – IR (acetone): $\tilde{\nu}$ = 2142, 2071, 2005, 1968 cm^{-1} (C≡O), 1768 (C=O). – ^{1}H NMR (80 MHz, [D$_6$]acetone): δ = 5.2 (m, CH_2). – ^{13}C{^{1}H} NMR (63 MHz, [D$_6$]acetone): δ = 187.49, 186.66 (s, C≡O), 161.68 (m, C=O), 101.45 (s, $RuC=CCH_2$), 90.01 (s, RuC=), 76.46 (s, CCl_3), 58.25, 57.21 (s, CH_2). – $C_{20}H_8Cl_{12}O_{12}Ru$ (966.8): calcd. C 24.85, H 0.83, Cl 44.01, Ru 10.45; found C 25.22, H 1.02, Cl 43.99, Ru 10.62.

5) *Tricarbonyl(η^4-hexamethyl benzenehexacarboxylate)osmium* (**7a**): To an ethylene-saturated solution of **6** (212 mg, 0.64 mmol) in 80 ml of *n*-hexane **2a** (285 mg, 2.00 mmol) was added dropwise. After stirring at room temp. for a few min a white solid precipitated. Cooling to −30°C, filtration (P3), and crystallization from *n*-hexane/acetone yielded 142 mg (32%) of **7a**, m.p. 68°C (dec.). – MS (FD), *m/z*: 702 [M$^+$, rel. to ^{192}Os]. – IR (KBr): $\tilde{\nu}$ = 2110, 2053, 2015 cm^{-1} (C≡O), 1762, 1729 (C=O). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.89 (s). – ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]acetone): δ = 178.96, 171.43 (s, C≡O), 168.60, 167.91, 163.33 (s, C=O), 148.56, 136.15, 130.34 (s, C=C), 52.62 (s, CH_3). – $C_{21}H_{18}O_{15}Os$ (700.6): calcd. C 36.00, H 2.59, Os 27.15; found C 35.61, H 3.22, Os 26.50.

6) *Tricarbonyl(η^4-hexaethyl benzenehexacarboxylate)osmium* (**7b**): To an ethylene-saturated solution of **6** (254 mg, 1.20 mmol) in 120 ml of *n*-hexane **2b** (652 mg, 3.83 mmol) was added dropwise. After stirring at room temp. for 8 h the reaction was complete. Cooling to −30°C, filtration (P3), and crystallization from *n*-hexane/acetone yielded 390 mg (41%) of **7b**, m.p. 93°C (dec.). – MS (FD), *m/z*: 786 [M$^+$, rel. to ^{192}Os]. – IR (KBr): $\tilde{\nu}$ = 2106, 2050, 2011 cm^{-1} (C≡O), 1738, 1723 (C=O). – ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.0–1.3 (m, 18H, CH_3), 3.8–4.3 (m, 12H, CH_2). – ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]acetone): δ = 177.06, 171.26 (s, C≡O), 169.06, 165.22, 163.57 (s, C=O), 151.90, 138.35, 134.24 (s, C=C), 48.85 (s, CH_2), 20.62 (s, CH_3). – $C_{27}H_{30}O_{15}Os$ (786.5): calcd. C 41.33, H 3.85, Os 24.24; found C 41.85, H 4.10, Os 23.55.

General Procedure for the Reaction of **7a**, **b** *with CO:* A solution of **7a**, **b** in ethyl methyl ketone was treated with CO (2 bar) in a pressure Schlenk tube at 50°C for 1 h. After removal of the solvent in vacuo the residue was suspended in diethyl ether, the suspension was filtered through a 2-cm silica column and the solvent removed in vacuo. The residue was dried in vacuo to give colorless crystals of **8a**, **b**.

7) *Hexamethyl Benzenehexacarboxylate* (**8a**): A solution of **7a** (120 mg, 0.17 mmol) in 20 ml of ethyl methyl ketone was allowed to react with CO, yielding 68 mg (93%) of **8a**, m.p. 192°C (ref.[13]

188°C). – MS (FD), *m/z*: 426 [M^+]. – IR (KBr): $\tilde{\nu}$ = 1739 cm^{-1} (C=O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.8 (ref.[13] 3.88). – $C_{18}H_{18}O_{12}$ (426.3): calcd. C 50.71, H 4.26; found C 51.32, H 4.50.

8) *Hexaethyl Benzenehexacarboxylate* (**8b**): A solution of **7b** (200 mg, 0.25 mmol) in 20 ml of ethyl methyl ketone was allowed to react with CO (2 bar), yielding 125 mg (96%) of **8b**, m.p. 38°C (ref.[13] 38°C). – MS (FD), *m/z*: 510 [M^+]. – IR (KBr): $\tilde{\nu}$ = 1737 cm^{-1} (C=O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 4.3 (q, ^1J = 7 Hz, 2H, CH_2) (ref.[13] 4.3), 1.3 (t, ^1J = 7 Hz, 3H, CH_3) (ref.[13] 1.33). – $C_{24}H_{30}O_{12}$ (510.5): calcd. C 56.47, H 5.92; found C 56.73, H 6.34.

☆ Dedicated to Professor *Reinhard Schmutzler* on the occasion of his 60th birthday.

[1] Part XC: E. Lindner, W. Wassing, M. W. Pitsch, R. Fawzi, M. Steimann, *Inorg. Chim. Acta*, in press.
[2] E. Müller, *Synthesis* **1974**, *23*, 761–774.
[3] K. P. C. Vollhardt, *Acc. Chem. Res.* **1977**, *10*, 1–8.
[4] Y. Wakatsuki, O. Nomura, K. Kitaura, K. Morokuma, H. Yamazaki, *J. Am. Chem. Soc.* **1983**, *105*, 1907–1912.
[5] P. Alphonse, F. Moyen, P. Mazerolles, *J. Organomet. Chem.* **1988**, *345*, 209–216.
[6] L. P. Yur'éva, *Russ. Chem. Rev. (Engl. Transl.)* **1974**, *43*, 48–68.
[7] W. Reppe, W. J. Schweckendiek, *Liebigs Ann. Chem.* **1948**, *560*, 104–116.
[8] H. Yamazaki, Y. Wakatsuki, *J. Organomet. Chem.* **1977**, *139*, 157–167.
[9] A. Funhoff, H. Schäufele, U. Zenneck, *J. Organomet. Chem.* **1988**, *345*, 331–339.
[10] A. F. Dyke, S. A. R. Knox, P. J. Naish, G. E. Taylor, *J. Chem. Soc., Dalton Trans.* **1982**, 1297–1307.
[11] P. M. Maitlis, *Pure Appl. Chem.* **1973**, *33*, 489–512.
[12] R. Burt, M. Cooke, M. Green, *J. Chem. Soc. (A)* **1970**, 2981–2986.
[13] E. Lindner, R.-M. Jansen, H. A. Mayer, W. Hiller, R. Fawzi, *Organometallics* **1989**, *8*, 2355–2360.
[14] E. Lindner, H. Kühbauch, *J. Organomet. Chem.* **1991**, *403*, C9–C14.
[15] F. W. Grevels, J. G. A. Reuvers, J. Takats, *J. Am. Chem. Soc.* **1981**, *103*, 4069–4073.
[16] G.-Y. Kiel, J. Takats, F. W. Grevels, *J. Am. Chem. Soc.* **1987**, *109*, 2227–2229.
[17] E. Lindner, E. Schauss, *Chem. Ber.* **1985**, *118*, 4292–4295.
[18] [18a] C. Bianchini, K. G. Caulton, C. Chardon, O. Eisenstein, K. Folting, T. J. Johnson, A. Meli, M. Peruzzini, D. J. Rauscher, W. E. Streib, F. Vizza, *J. Am. Chem. Soc.* **1991**, *113*, 5127–5129. – [18b] R. L. Thompson, S. Lee, A. L. Rheingold, N. J. Cooper, *Organometallics* **1991**, *10*, 1657–1659.
[19] A. Bader, Ph. D. Thesis, University of Tübingen, **1990**.
[20] C. E. L. Headford, W. R. Roper, *J. Organomet. Chem.* **1980**, *198*, C7–C10.

[9/94]