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Binuclear Metal Carbonyl DAB Complexes. 10. Activation of η^2-C=N-Coordinated DAB Ligands toward C—C Bond Formation with Alkynes. X-ray Structure of [2-Phenyl-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl]diruthenium Pentacarbonyl. Application to the Catalytic Cyclotrimerization of Alkynes

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$Ru_2(CO)_6(DAB)$ (DAB = 1,4-diazabutadiene) complexes react with alkynes forming $Ru_2(CO)_5(AIB)$ complexes (AIB = 3-amino-4-imino-1-buten-1-yl). In these products the DAB ligand and the alkyne are coupled via a C–C bond. The molecular structure of these complexes has been determined by a single-crystal X-ray study. Cell data are a = 12.411 (2) Å, b = 16.137 (3) Å, c = 12.487 (2) Å, and β = 92.78 (2)°; the space group is $P2_1/n$, and Z = 4. The refinement converged to R = 4.4%. The molecular structure of [2-phenyl-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl]diruthenium pentacarbonyl established a C–C single bond of 1.546 (10) Å between the original DAB and the phenylacetylene fragments. The $Ru_2(CO)_5$ unit contains four terminal and one bridging CO groups. The Ru–Ru bond distance is 2.711 (1) Å, which is in accordance with a single Ru–Ru bond. The coordination around the ruthenium atoms is pseudooctahedral, disregarding the metal–metal interaction. Taking into account the Ru–Ru bond, we find that both ruthenium atoms are seven-coordinated. $Ru_2(CO)_5(AIB)$ complexes react with alkynes forming $Ru_2(CO)_5(AIB)$(alkyne) and subsequently $Ru_2(CO)_4(AIB)$(alkyne) complexes. According to the spectroscopic data, the alkyne in the former complex acts as a 2e-donor ligand and in the latter complex as a 4e-donor ligand, bridging the $Ru_2(CO)_4$ unit. $Ru_2(CO)_6(DAB)$, $Ru_2(CO)_5(AIB)$, $Ru_2(CO)_5(AIB)$(alkyne), and $Ru_2(CO)_4(AIB)$(alkyne) can all be used as a catalyst for the cyclotrimerization of acetylenes. The reaction has to be carried out at 110 °C and is terminated after a maximum of 380 cycles. The catalytic conversions have been monitored by high-pressure liquid chromatography, and it could be shown that the actual catalyst is formed out of $Ru_2(CO)_4(AIB)$(alkyne). Experiments with deuterated alkynes in the complexes evidenced that these coordinated alkynes are not involved in the (substituted) benzene formation. The cyclotrimerization of methyl acetylenecarboxylate results in the formation of 1,3,5-tris(methoxycarbonyl)benzene exclusively. This regioselectivity is an uncommon feature in catalytic alkyne trimerization.

Introduction

We have recently shown that the activation of the C=N double bonds of 1,4-diazabutadienes (DAB) can be achieved by η^2-C=N coordination of the ligand. This has been shown for $Ru_2(CO)_6(DAB)$ complexes, containing a σ-N,μ^2-N′,η^2-C=N′-coordinated DAB ligand acting as a 6e donor with respect to the binuclear carbonyl fragment.[1] Reaction of these complexes with uncoordinated DAB ligands produced $Ru_2(CO)_5(IAE)$ complexes (IAE = bis[(alkylamino)(alkylimino)ethane]) in which two DAB ligands are linked via a C–C bond between two imine carbon atoms, thus forming the IAE ligand.

An earlier example of such a C–C bond formation between two coordinated DAB ligands was observed in a redox reaction of $Mo(CO)_4(DAB)$, resulting in $Mo_2(CO)_6(IAE)$ production. The structure of this latter complex was determined by means of X-ray diffraction.[2] It was postulated that in the mechanism for $Mo_2(CO)_6(IAE)$ formation, the production of an η^2-C=N-coordinated species would be the activating step. The isolation of $Ru_2(CO)_6(DAB)$ as intermediates in the formation of $Ru_2(CO)_5(IAE)$ complexes provided evidence for this hypothesis.[1]

General consideration on the mechanism of the C–C bond formation between a coordinated activated DAB ligand and an uncoordinated DAB molecule led to the conclusion that the σ-N,μ^2-N′,η^2-C=N′-coordinated DAB ligands in $M_2(CO)_6(DAB)$ complexes (M = Fe,[3,4] Ru,[1] Os;[5] M = Mn, Re and M′ = Co[6]) should be activated toward C–C bond formation with a variety of unsaturated small molecules. We therefore investigated the reactions between a series of alkynes and $Ru_2(CO)_6(DAB)$ complexes, and C–C bond formation between an imine carbon atom and an acetylene carbon atom is indeed observed.

Experimental Section

^{1}H NMR spectra were recorded with a Varian T 60 spectrometer, IR spectra with a Perkin-Elmer 283 spectrophotometer, field-desorption mass spectra with a Varian 711 spectrometer, and electron-impact mass spectra with a MS 902 mass spectrometer.

$Ru_3(CO)_{12}$ and alkynes were obtained from commercial sources. Dimethyl acetylenedicarboxylate was distilled prior to use.

All solvents were dried and distilled prior to use with the exception of the eluant used for high-pressure liquid chromatography.

High-pressure liquid chromatography was carried out with a homemade device using an Orlita TW 1 high-pressure liquid pump and a Du Pont UV detector operating at 280 nm. Continued sampling of the reaction mixture was done with the use of a Gilson Minipuls II peristaltic pump.

$Ru_2(CO)_6(DAB)$ (compound I; see Figure 9) was prepared according to standard procedures.[1] Reactions were carried out in a purified nitrogen atmosphere.

Elemental analyses were carried out by the Section Elemental Analyses of the Institute for Organic Chemistry, TNO, Utrecht, The Netherlands.

Preparation of $Ru_2(CO)_5(AIB)$[7] [AIB = 2-Phenyl-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl, 2-*p*-Tolyl-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl] (IIa, IIb; See Figure 9). $Ru_2(CO)_6$[glyoxal bis(*tert*-butylimine)] (Ia) (1.0 mmol) and RC≡CH (1.0 mmol, R = phenyl, *p*-tolyl) were refluxed in 20 mL of heptane

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(1) Staal, L. H.; Polm, L. H.; Balk, R. W.; van Koten, G.; Vrieze, K.; Brouwers, A. M. F. *Inorg. Chem.* **1980**, *19*, 3343-3351.

(2) Staal, L. H.; Oskam, A.; Vrieze, K.; Roosendaal, E.; Schenk, H. *Inorg. Chem.* **1979**, *18*, 1634-1640.

(3) Frühauf, H. W.; Landers, A.; Goddard, R.; Krüger, C. *Angew. Chem.* **1978**, *90*, 56-57.

(4) Staal, L. H.; Keijsper, J.; Polm, L. H.; Vrieze, K. *J. Organomet. Chem.* **1981**, *204*, 101-113.

(5) Staal, L. H.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *206*, 99-108.

(6) Staal, L. H.; Keijsper, J.; van Koten, G.; Vrieze, K.; Cras, J. A.; Bosman, W. *Inorg. Chem.* **1981**, *20*, 555-562.

(7) AIB has been chosen as the abbreviation for the molecules derived from C–C bond formation between a DAB ligand and an alkyne. The backbone of these ligands is RN=CHCH(NR)(R′)C=(R″) which is a 3-amino-4-imino-1-butene. This name is not the proper systematic name since the alkene substituents should take part in the naming of the skeleton. 2-Phenyl-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl, should be named 6,6-dimethyl-2-phenyl-3-(*tert*-butylamino)-5-azahepta-1,4-dien-1-yl. However, AIB is a comprehensive naming, and additional naming of the substituents will show the relation between these systems better than using the correct IUPAC nomenclature.

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for 1.5 h, after which the yellow solution changed to red. The solution was concentrated to 4 mL, and a red oil precipitated. The remaining solvent was removed by decantation, and 10 mL of pentane and 0.5 mL of ethanol were added to the oil. After 1 h of violent shaking and stirring, the red oil changed into a red solid precipitate. The precipitate was filtered off and was recrystallized from diethyl ether/pentane (10:3) at −70 °C to produce red crystals in 60% yield.

Preparation of $Ru_2(CO)_5$(AIB) [AIB = 2-*tert*-Butyl-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl] (IIc; See Figure 9). $Ru_2(CO)_6$[glyoxal bis(*tert*-butylimine)] (Ia) and *t*-BuC≡CH were refluxed in 30 mL of heptane for 72 h. The solution was allowed to cool and was filtered to remove a yellow precipitate. The filtrate was evaporated to dryness. The product was separated from the crude mixture by column chromatography using silica (Merck 60) as the stationary phase. Hexane/diethyl ether (10:1 v/v) was used as eluant to extract the unreacted starting material from the column. $Ru_2(CO)_5$(AIB) was obtained as a red-orange fraction by using dichloromethane as an eluant. The dichloromethane fraction was evaporated to dryness, and the solid residue was recrystallized from diethyl ether/pentane (10:3) at −70 °C to produce orange needles in a very low yield (less than 5%). The yellow precipitate mentioned above consisted of $Ru_2(CO)_5$(IAE) according to the comparison of the spectral data with the literature values.[1]

Preparation of $Ru_2(CO)_5$(AIB) [AIB = 1,2-Bis(methoxycarbonyl)-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl, 1,2-Bis(methoxycarbonyl)-3-(isopropylamino)-4-(isopropylimino)-1-buten-1-yl] (IId, IIe; See Figures 4 and 9). $Ru_2(CO)_6$(DAB) [DAB = glyoxal bis(*tert*-butylimine) (Ia), glyoxal bis(isopropylimine) (Ib)] (1.0 mmol), and dimethyl acetylenedicarboxylate were stirred for 3 h in 30 mL of toluene. During the reaction the color changed from yellow into red. The solution was concentrated to 2 mL, and 15 mL of pentane was added. A red solid precipitated, and the solvent was decanted. The precipitate was washed twice by stirring it violently for 10 min with 10 mL of pentane and was filtered off. The pure product was obtained in 80% yield by recrystallization from diethyl ether at −70 °C.

$Ru_2(CO)_5$(AIB) [AIB = 2-(Methoxycarbonyl)-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl] (IIf; See Figures 4 and 9). $Ru_2(CO)_6$[glyoxal bis(*tert*-butylimine)] (Ia) (1.0 mmol) and methlyl acetylenecarboxylate (1.0 mmol) were refluxed for 3 h in 30 mL of toluene. The pure product was obtained via the procedure described above for the dimethyl acetylenedicarboxylate derivatives, in 70% yield.

$Ru_2(CO)_5$(AIB)(dimethyl acetylenedicarboxylate) [AIB = 1,2-Bis(methoxycarbonyl)-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl, 1,2-Bis(methoxycarbonyl)-3-(isopropylamino)-4-(isopropylimino)-1buten-1-yl, 1,2-Bis(methoxycarbonyl)-3-(cyclohexylamino)-4-(cyclohexylimino)-1-buten-1-yl] (IIIa, IIIb, IIIc; See Figure 9). Method A. $Ru_2(CO)_6$(DAB) (1.0 mmol) [DAB = glyoxal bis(*tert*-butylimine) (Ia), glyoxal bis(isopropylimine) (Ib), glyoxal bis(cyclohexylimine) (Ic)] and dimethyl acetylenedicarboxylate (2.0 mmol) were stirred for 3 h in 20 mL of toluene. During the reaction a yellow orange precipitate was formed. The solution was concentrated to 5 mL, and 10 mL of pentane was added to achieve complete precipitation of the crude product. The solvent was decanted from the yellow solid which was washed twice with 10 mL of diethyl ether by stirring it violently. A pale yellow product was obtained by filtration. Recrystallization from dichloromethane/pentane (2:1) at −70 °C gave the pure product in 90% yield.

Method B. $Ru_2(CO)_5$(AIB) (1.0 mmol) and dimethyl acetylenedicarboxylate (1.0 mmol) were used as the starting materials. The procedures for the working up of the reaction mixtures were as described for method A.

Preparation of $Ru_2(CO)_4$(AIB)(dimethyl acetylenedicarboxylate) [AIB = 1,2-Bis(methoxycarbonyl)-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl] (IVa). $Ru_2(CO)_6$[glyoxal bis(*tert*-butylimine)] (Ia) (1.0 mmol) and dimethyl acetylenedicarboxylate (2.0 mmol) were refluxed for 3 h in heptane. A yellow precipitate was filtered off which was washed twice with 10 mL of heptane. Recrystallization form dichloromethane/diethyl ether (2:1 v/v) yielded the pure product in 60% yield.

Preparation of $Ru_2(CO)_4$(AIB)(dimethyl acetylenedicarboxylate) [AIB = 2-Phenyl-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl] (IVb; See Figure 9). $Ru_2(CO)_5$(AIB) (IIa) (1.0 mmol) and dimethyl acetylenedicarboxylate (3 mmol) were refluxed for 1 h in 30 mL of toluene. The solvent was removed under vacuum, and the residue was washed twice with 30 mL of diethyl ether. Recrystallization of the residue from 5 mL of dichloromethane/pentane (2:1 v/v) at −70 °C gave the product in less than 10% yield.

Hexadeuteriodimethyl Acetylenedicarboxylate. This method is a modification of the method published by Collman et al.[8] Acetylenedicarboxylic acid (4.0 g, 34 mmol) was added to a solution of methanol-d_4 (5 mL) and concentrated sulfuric acid (4.5 mmol) at −10 °C. The mixture was stirred for 2 h at 70 °C and was allowed to cool. Water (20 mL) was added, and the mixture was extracted five times with 50 mL of diethyl ether. The ether fractions were collectively washed with 200 mL of water, 20 mL of a saturated aqueous sodium bicarbonate solution, and finally with 200 mL of water. The ether fraction was dried by stirring with $MgSO_4$, and the solvent was removed under vacuum. A yellow oil was left behind from which 2.8 g of hexadeuteriodimethyl acetylenedicarboxylate could be obtained by vacuum distillation (70 °C (3 mm)). The product was characterized by mass spectrometry, and the molecular ion was observed at m/z 148 (calcd 148), while m/z 142 was absent.

Preparation of Deuterated Complexes. Deuterated complexes have been prepared according to the methods described above starting from hexadeuteriodimethyl acetylenedicarboxylate. The complexes have been characterized by FD mass spectrometry, and the results are listed in Table I.

Preparation of Hexakis(methoxycarbonyl)benzene. $Ru_2(CO)_6$[glyoxal bis(*tert*-butylimine)] (1.0 mmol) and dimethyl acetylenedicarboxylate (10 mL) were refluxed in 40 mL of toluene for 12 h. The reaction mixture was allowed to cool and turned solid at room temperature. Pentane (100 mL) was added, and the mixture was stirred to produce a yellowish precipitate. The precipitate was filtered off and was twice recrystallized from dichloromethane at −70 °C to give 9.3 g of the pure product (80%).

Preparation of 1,3,5-Tris(methoxycarbonyl)benzene (Experiment A). $Ru_2(CO)_6$[glyoxal bis(*tert*-butylimine)] (1.0 mmol) and methyl acetylenecarboxylate (2 g) were refluxed for 13 h in toluene. After the reaction, the reaction mixture was evaporated to dryness. The residue was extracted four times with 50 mL of diethyl ether, and the combined fractions were concentrated to 30 mL. Crystallization at −70 °C produced white crystals of the crude product. Recrystallization at −70 °C from diethyl ether gave the pure product in 90% yield.

Application of $Ru_2(CO)_5$[1,2-bis((trideuteriomethoxy)carbonyl)-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl] (IId) as a Catalyst for Cyclotrimerization of Dimethyl Acetylenedicarboxylate (Experiment B). $Ru_2(CO)_5$(AIB-d_6) (IId) (0.5 mmol) and dimethyl acetylenedicarboxylate (5 mmol) were refluxed for 2 h in 10 mL of toluene. Hexakis(methoxycarbonyl)benzene was isolated by means of extraction with diethyl ether and was purified as described above. The residue was separated on a silica column using dichloromethane as the eluant. The yellow fraction was collected and was recrystallized at −70 °C to give a mixture of $Ru_2(CO)_5$[(AIB-d_6)(dimethyl acetylenedicarboxylate)] (IIIa) and $Ru_2(CO)_4$[(AIB-d_6)(dimethyl acetylenedicarboxylate)] (IVa). The isotopic distribution has been determined with EI MS for the hexakissubstituted benzene and with FD MS for the recovered catalysts. The results are included in Table I.

Application of $Ru_2(CO)_5$[1,2-bis((trideuteriomethoxy)carbonyl)-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl][hexadeuteriodimethyl acetylenedicarboxylate] (IIIa) as a Catalyst for the Cyclotrimerization of Dimethyl Acetylenedicarboxylate (Experiment C). $Ru_2(CO)_5$[(AIB-d_6)(dimethyl-d_6 acetylenedicarboxylate)] (IIIa) (0.5 mmol) and dimethyl acetylenedicarboxylate (5 mmol) were refluxed for 2 h in 10 mL of toluene. The procedure discussed above was applied to isolate and characterize the compounds.

High-Pressure Liquid Chromatography Experiments. The reaction conditions for the high-pressure liquid chromatography are briefly outlined in Table II.

All the complexes gave molecular ions in the FD mass spectra in agreement with the calculated molecular weights. The results for deuterated complexes are included in Table I.

Crystal Structure Determination of [2-Phenyl-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl]diruthenium Pentacarbonyl (IIa). Monoclinic crystals were obtained from a dichloromethane solution at −70 °C. Cell constants measured at room temperature

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(8) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298–1303.

Table I. FD/MS and EI/MS Data of Deuterated Compounds and Tricyclomerization Products (Values for Nondeuterated Compounds in Parentheses)

compd	M_r (calcd)[a]	M^+ (M/Z)[b]
Deuterated Compounds		
$Ru_2(CO)_5$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C)($CD_3O_2CC{\equiv}CCO_2CD_3$) (IIIa)	800 (794)	801 (795)
$Ru_2(CO)_5$(AIB; *t*-Bu,CD_3O_2C,CD_3O_2C)($CH_2O_2CC{\equiv}CCO_2CH_3$) (IIIa)	800 (794)	801 (795)
$Ru_2(CO)_5$(AIB; *t*-Bu,CD_3O_2C,CD_3O_2C) (IIIa)	658 (652)	659 (653)
$Ru_2(CO)_4$(AIB; *t*-Bu,CD_3O_2C,CD_3O_2C)($CD_3O_2CC{\equiv}CCO_2CD_3$) (IVa)	772 (766)	773 (767)
$CD_3COOCC{\equiv}CCOOCD_3$	148 (142)	148 (142)
Trimerization Products		
$(CH_3O_2C)_6C_6$ expt A	426	426
expt B	426	426
expt C	426	426
$(CH_3O_2C)_3C_6H_3$	252	252

[a] Molecular weight based upon ^{101}Ru. [b] Highest peak of the isotropic pattern.

Table II. Reaction Conditions of the Catalytic Trimerizations As Studied by Means of High-Pressure Liquid Chromatography[a]

catalyst	amt of catalyst, mg	amt of alkyne,[b] mL	*t*, °C	time, h	cycles[c]
$Ru_2(CO)_5$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C) (IId)	20	1	100	24	21
$Ru_2(CO)_5$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$) (IIIa)	6.5	0.5	110	8	136
	20	1.0	40	2	0
	20	1.0	70	2	0
$Ru_2(CO)_5$(AIB; *i*-Pr,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$) (IIIb)	30	1.0	100	19	62
$Ru_2(CO)_5$(AIB; *t*-Bu,phenyl,H)	12	0.5	110	5	68
$Ru_2(CO)_4$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$)	0.9	0.5	110	8	380

[a] Reactions were carried out in 30 mL of toluene. [b] Alkyne = $CH_3O_2CC{\equiv}CCO_2CH_3$. [c] Mole of hexakis(methoxycarbonyl)benzene per mole of catalyst.

Table III. Atomic Coordinates (Esd's in Parentheses)

	x	*y*	*z*		*x*	*y*	*z*
Ru(1)	0.20212 (5)	0.22955 (4)	0.27224 (5)	O(3)	0.2382 (6)	0.1820 (6)	0.5006 (5)
Ru(2)	0.03395 (4)	0.26300 (3)	0.39586 (4)	O(4)	0.0769 (8)	0.3830 (6)	0.5778 (7)
C(1)	0.2816 (8)	0.1383 (7)	0.2304 (8)	O(5)	−0.0474 (7)	0.1400 (5)	0.5608 (6)
C(2)	0.3324 (8)	0.2842 (8)	0.2964 (10)	H(61)	0.152 (5)	0.396 (4)	0.295 (5)
C(3)	0.1854 (6)	0.2099 (6)	0.4296 (7)	H(81)	−0.018 (6)	0.234 (4)	0.093 (6)
C(4)	0.0561 (8)	0.3381 (6)	0.5091 (7)	H(91)	−0.176 (7)	0.297 (6)	0.160 (7)
C(5)	−0.0233 (7)	0.1847 (5)	0.4948 (6)	H(111)	−0.127 (6)	0.411 (5)	0.475 (7)
C(6)	0.1019 (6)	0.3468 (5)	0.2836 (6)	H(122)	−0.160 (5)	0.458 (5)	0.351 (6)
C(7)	0.0706 (6)	0.3288 (4)	0.1815 (5)	H(113)	−0.255 (5)	0.450 (5)	0.436 (6)
C(8)	−0.0107 (6)	0.2562 (4)	0.1736 (6)	H(121)	−0.271 (6)	0.228 (4)	0.409 (6)
C(9)	−0.1141 (5)	0.2896 (5)	0.2164 (6)	H(122)	−0.195 (7)	0.272 (5)	0.501 (7)
C(10)	−0.2198 (6)	0.3373 (5)	0.3628 (7)	H(123)	−0.324 (5)	0.301 (5)	0.482 (5)
C(11)	−0.1854 (9)	0.4215 (6)	0.4109 (9)	H(131)	−0.288 (6)	0.393 (5)	0.229 (6)
C(12)	−0.2520 (9)	0.2792 (7)	0.4494 (9)	H(132)	−0.328 (4)	0.289 (3)	0.252 (5)
C(13)	−0.3102 (7)	0.3476 (8)	0.2791 (9)	H(133)	−0.376 (6)	0.366 (5)	0.314 (6)
C(14)	−0.0026 (7)	0.1069 (5)	0.2294 (7)	H(151)	−0.008 (6)	0.108 (5)	0.073 (6)
C(15)	0.0276 (10)	0.0768 (6)	0.1162 (9)	H(152)	0.110 (5)	0.083 (5)	0.119 (6)
C(16)	0.0482 (9)	0.0483 (5)	0.3110 (9)	H(153)	0.011 (5)	0.017 (5)	0.104 (6)
C(17)	−0.1259 (8)	0.1029 (6)	0.2339 (8)	H(161)	0.134 (6)	0.053 (5)	0.306 (7)
C(18)	0.0926 (6)	0.3787 (5)	0.0831 (6)	H(162)	0.027 (7)	0.062 (6)	0.391 (8)
C(19)	0.0235 (6)	0.3751 (6)	−0.0079 (6)	H(163)	0.032 (6)	−0.007 (6)	0.292 (7)
C(20)	0.0486 (8)	0.4204 (7)	−0.0979 (8)	H(171)	−0.146 (8)	0.117 (6)	0.303 (8)
C(21)	0.1413 (8)	0.4680 (6)	−0.0977 (8)	H(172)	−0.169 (6)	0.143 (5)	0.173 (6)
C(22)	0.2102 (8)	0.4696 (6)	−0.0097 (8)	H(173)	−0.147 (7)	0.035 (7)	0.221 (8)
C(23)	0.1879 (7)	0.4254 (5)	0.0819 (7)	H(19)	−0.036 (6)	0.348 (6)	−0.012 (7)
N(1)	−0.1184 (5)	0.3022 (4)	0.3156 (5)	H(20)	0.000 (6)	0.424 (4)	−0.154 (6)
N(2)	0.0389 (5)	0.1929 (4)	0.2483 (5)	H(21)	0.157 (5)	0.500 (5)	−0.164 (6)
O(1)	0.3305 (7)	0.0811 (6)	0.2042 (7)	H(22)	0.277 (6)	0.500 (5)	−0.007 (7)
O(2)	0.4111 (7)	0.3197 (8)	0.3182 (10)	H(23)	0.242 (6)	0.423 (5)	0.144 (6)

are a = 12.411 (2) Å, b = 16.137 (2) Å, c = 12.487 (2) Å, β = 92.78 (2)°, and Z = 4. From the systematic extinctions it was concluded that the spacegroup is $P2_1/n$.

A total of 3964 reflections with $I > 2.5\sigma(I)$ were measured on a Monius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. An absorption correction was applied (crystal dimension 0.1 × 0.2 × 0.25 mm; μ = 12.2 cm^{-1}). An E^2-Patterson syntheses yielded the positions of the two Ru atoms in the asymmetric unit. From a eightfold Patterson minimum function based on the eight ruthenium positions in the unit cell, the remaining nonhydrogen atoms were obtained. Refinement was carried out by means of anisotropic block-diagonal least-squares calculation and converged to R = 4.4% for 3964 observed reflections. The hydrogen atoms were located in a ΔF synthesis and were included with isotropic temperature factors in the final cycles of refinement. In the last refinement cycle, the ratio of largest shift to standard deviation was less than 1 for the coordinates and for the thermal parameters of the nonhydrogen atoms and less than 2 for the thermal parameters of the Ru atoms. A final difference map was computed, which was featureless except for positive areas of about 1 e/Å^3 near both Ru atoms.

A weighting scheme $w = [2.8 + F_o + 0.036F_o^2]$ was used, and the anomalous scattering of Ru was taken into account. Atomic scattering

Table IV. Selected Bond Distances (Å) of the Nonhydrogen Atoms

Ru(1)-Ru(2)	2.711 (1)	Ru(2)-N(1)	2.190 (6)	C(8)-N(2)	1.496 (9)
Ru(1)-C(1)	1.861 (11)	Ru(2)-N(2)	2.166 (6)	C(9)-N(1)	1.259 (10)
Ru(1)-C(2)	1.853 (11)	C(1)-O(1)	1.160 (14)	C(10)-N(1)	1.524 (10)
Ru(1)-C(3)	2.011 (9)	C(2)-O(2)	1.154 (15)	C(14)-N(2)	1.495 (10)
Ru(1)-C(6)	2.273 (8)	C(3)-C(3)	1.167 (11)	C(18)-C(19)	1.391 (10)
Ru(1)-C(7)	2.528 (10)	C(4)-O(4)	1.143 (13)	C(18)-C(23)	1.403 (11)
Ru(1)-N(2)	2.118 (6)	C(5)-O(5)	1.146 (11)	C(19)-C(20)	1.389 (13)
Ru(2)-C(3)	2.090 (8)	C(6)-C(7)	1.346 (10)	C(20)-C(21)	1.383 (14)
Ru(2)-C(4)	1.872 (9)	C(7)-C(8)	1.546 (10)	C(21)-C(22)	1.360 (14)
Ru(2)-C(5)	1.927 (8)	C(7)-C(18)	1.505 (10)	C(22)-C(23)	1.387 (13)
Ru(2)-C(6)	2.149 (8)	C(8)-C(9)	1.513 (10)		

Table V. Selected Bond Angles (Deg) (Esd's in Parentheses) of the Nonhydrogen Atoms

C(1)-Ru(1)-Ru(2)	138.8 (3)	C(3)-Ru(2)-N(2)	84.0 (3)	Ru(2)-C(3)-O(3)	141.1 (7)
C(1)-Ru(1)-C(2)	87.2 (5)	C(4)-Ru(2)-Ru(1)	118.1 (3)	Ru(2)-C(4)-O(4)	175.4 (9)
C(1)-Ru(1)-C(3)	103.3 (4)	C(4)-Ru(2)-C(5)	89.2 (4)	Ru(2)-C(5)-O(5)	172.4 (8)
C(1)-Ru(1)-C(6)	167.3 (4)	C(4)-Ru(2)-C(6)	92.1 (4)	Ru(1)-C(6)-Ru(2)	75.5 (3)
C(1)-Ru(1)-N(2)	104.8 (4)	C(4)-Ru(2)-N(1)	104.5 (3)	Ru(1)-C(6)-C(7)	84.0 (5)
C(2)-Ru(1)-Ru(4)	120.2 (4)	C(4)-Ru(2)-N(2)	166.3 (3)	Ru(2)-C(6)-C(7)	112.2 (5)
C(2)-Ru(1)-C(3)	92.7 (4)	C(5)-Ru(2)-Ru(1)	123.4 (3)	C(6)-C(7)-C(8)	112.4 (6)
C(2)-Ru(1)-C(6)	94.0 (4)	C(5)-Ru(2)-C(6)	177.8 (3)	C(6)-C(7)-C(19)	127.0 (7)
C(2)-Ru(1)-N(2)	167.6 (4)	C(5)-Ru(2)-N(1)	98.4 (3)	C(8)-C(7)-C(18)	119.8 (6)
C(3)-Ru(1)-Ru(2)	49.8 (2)	C(5)-Ru(2)-N(2)	103.3 (3)	C(7)-C(8)-C(9)	105.6 (6)
C(3)-Ru(1)-C(6)	89.3 (3)	C(6)-Ru(2)-Ru(1)	54.2 (2)	N(2)-C(8)-C(9)	110.7 (6)
C(3)-Ru(1)-N(2)	87.2 (3)	C(6)-Ru(2)-N(1)	82.9 (3)	N(2)-C(8)-C(7)	103.3 (6)
C(6)-Ru(1)-Ru(2)	50.1 (2)	C(6)-Ru(2)-N(2)	75.3 (3)	C(8)-C(9)-N(1)	118.8 (6)
C(6)-Ru(1)-N(2)	73.7 (3)	N(1)-Ru(2)-Ru(1)	118.0 (2)	C(9)-N(1)-Ru(2)	109.1 (5)
N(2)-Ru(1)-Ru(2)	51.5 (2)	N(1)-Ru(2)-N(2)	79.7 (2)	C(9)-N(1)-C(10)	121.0 (6)
C(3)-Ru(2)-Ru(1)	47.4 (3)	N(2)-Ru(2)-Ru(1)	50.0 (2)	C(10)-N(1)-Ru(2)	129.9 (5)
C(3)-Ru(2)-C(4)	90.9 (4)	Ru(1)-C(1)-O(1)	179.5 (9)	C(8)-N(2)-Ru(1)	105.0 (4)
C(3)-Ru(2)-C(5)	87.6 (4)	Ru(1)-C(2)-O(2)	175.3 (11)	C(8)-N(2)-C(14)	114.0 (6)
C(3)-Ru(2)-C(6)	90.7 (3)	Ru(1)-C(3)-Ru(2)	82.7 (3)	C(14)-N(2)-Ru(1)	127.0 (5)
C(3)-Ru(2)-N(1)	163.5 (3)	Ru(1)-C(3)-O(3)	136.2 (7)		

factors and dispersion corrections were taken from ref 10. Computer programs have been taken from the X-RAY system (1976).[9]

The final coordinates are listed in Table III; thermal parameters and a list of observed and calculated structure factor amplitudes have been submitted as supplementary material.

Results

Molecular Structure of [2-Phenyl-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl]diruthenium Pentacarbonyl (Compound IIa). The molecular structure of [2-phenyl-3-(*tert*-butylamino)-4-(*tert*-butylimino)-1-buten-1-yl]diruthenium pentacarbonyl (abbreviated throughout this paper as $Ru_2(CO)_5$(AIB; *t*-Bu,phenyl,H) (IIa); other related complexes have been abbreviated similarly) is shown in Figure 1 and a stereoview in Figure 2. The bond lengths and bond angles are listed in Tables IV and V, respectively.

The Ru(1)-Ru(2) distance of 2.711 (1) Å is short for a ruthenium–ruthenium single bond. Values of 2.735 (2) and 2.740 (4), Å have been reported,[11,12] but bond lengths near 2.8-2.9 Å are more generally observed.[13-21]

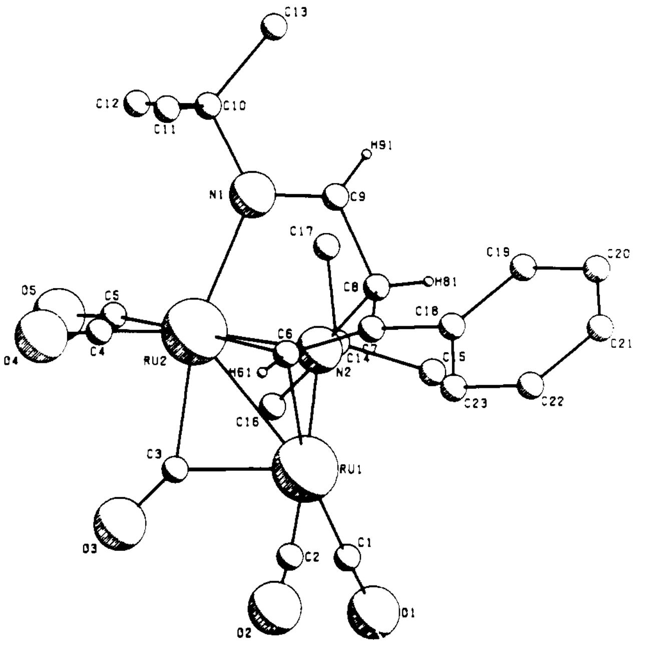

Figure 1. Molecular structure of $Ru_2(CO)_5$(AIB; *t*-Bu,phenyl,H) showing the atomic numbering. Lewis structure is shown as part of the scheme in Figure 9 (II).

The metal–carbonyl unit consists of four terminal and one bridging carbonyl groups. The bridging carbonyl group is bonded via C(3) to Ru(1) and Ru(2) with bond distances of 2.011 (9) and 2.009 (8) Å, respectively. The angles around

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(9) Stewart, J. M. Technical Report TR-446; Computer Science Center, University of Maryland: College Park, Md, 1976.

(10) "International Tables for X-ray Crystallography"; Kynoch Press: Brimingham, England, 1974; Vol. IV.

(11) Mills, O. S.; Nice, J. P. *J. Organomet. Chem.* **1967**, *9*, 339–344.

(12) Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1973**, *12*, 191–198.

(13) Gamline, O.; Sappa, E.; Manotti Lanfredi, A. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1979**, *36*, 189–195.

(14) Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1973**, 912–913.

(15) Goddard, R.; Humphries, A. P.; Knox, S. A. R.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1975**, 507–508.

(16) Bruce, M. I.; Howard, J.; Knox, S. A. R.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1972**, 1041–1042.

(17) Cotton, F. A.; Edwards, W. T. *J. Am. Chem. Soc.* **1968**, *90*, 5412–5417.

(18) Cotton, F. A.; Hanson, B. E.; Jamerson, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 6588–6594.

(19) Mason, R.; Robinson, W. R. *Chem. Commun.* **1968**, 468–469.

(20) Bau, R.; Burt, J. C.; Knox, S. A. R., Laine, R. M.; Philips, R. D.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 726–727.

(21) Bau, R.; Chou, B. C.; Knox, S. A. R.; Riera, V.; Stone, F. G. A. *J. Organomet. Chem.* **1974**, *82*, C43–C47.

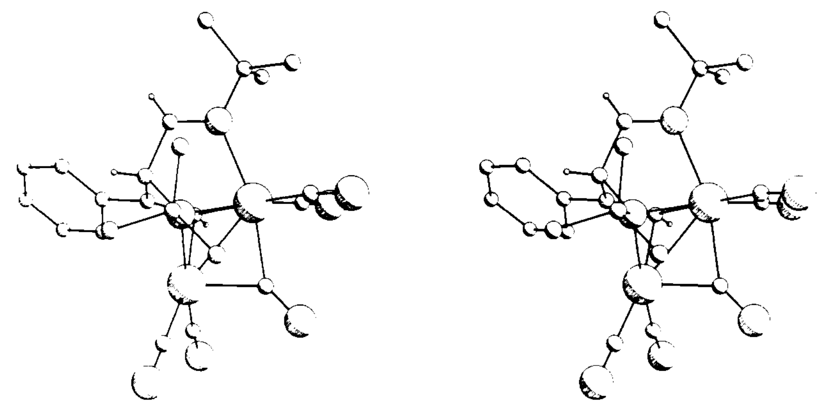

Figure 2. Stereoview of the molecule.

Table VI. ν(CO) Frequencies of $Ru_2(CO)_5$(AIB), $Ru_2(CO)_5$(AIB)(alkyne), and $Ru_2(CO)_4$(AIB)(alkyne) Complexes

R,R′,R″	σ-CO	μ-CO	CH_3O_2C
	$Ru_2(CO)_5$(AIB; R,R′,R″) (II)		
t-Bu,phen,H[a] (IIa)	2035, 2002, 1976, 1939	1828	
t-Bu,*p*-tol,H[a] (IIb)	2044, 2032, 1975, 1937	1827	
t-Bu,*t*-Bu,H[a] (IIc)	2056, 2034, 1973, 1936	1829	
t-Bu,CH_3O_2C,H[a] (IIf)	2040, 2010, 1981, 1941	1841	1697[b]
t-Bu,CH_3O_2C,CH_3O_2C[a] (IId)	2049, 2023, 1982, 1951	1844 (1828[b])	1709
i-Pr,CH_3O_2C,CH_3O_2C[b] (IIc)	2044, 2012, 1986, 1946	1827	1704
	$Ru_2(CO)_5$(AIB; R,R′,R″)(alkyne)[c] (III)		
t-Bu,CH_3O_2C,CH_3O_2C[b] (IIIa)	2085, 2033, 2016, 1976		1734, 1700
i-Pr,CH_3O_2C,CH_3O_2C[b] (IIIb)	2087, 2034, 2016, 1976		1734, 1698
c-Hx,CH_3O_2C,CH_3O_2C[b] (IIc)	2083, 2031, 2012, 1973		1734, 1697
	$Ru_2(CO)_4$(AIB; R,R′,R″)(alkyne)[c] (IV)		
t-Bu,CH_3O_2C,CH_3O_2C[b] (IVa)	2060, 2028, 2005, 1976		1700
t-Bu,phen,H[b] (IVb)	2044, 2019, 1982, 1956		1709

[a] Solvent is pentane. [b] Solvent is dichloromethane. [c] Alkyne is $CH_3O_2CC{\equiv}CCO_2CH_3$.

C(3) are Ru(1)–C(3)–Ru(2) 82.7 (3), Ru(1)–C(3)–O(3) 136.2 (2), and Ru(2)–C(3)–O(3) 141.1 (7)°, demonstrating that this carbonyl group is symmetrically bridging the two ruthenium atoms.[22]

The organic molecule coordinated to the metal carbonyl moiety is formed from one 1,4-diazabutadiene (DAB) and one phenylacetylene ligand and is linked by a C–C single bond of 1.546 (10) Å between C(7) and C(8). Consequently C(8)–N(2) has been reduced to a single bond which is reflected by the bond distance of 1.496 (9) Å. The C(9)–N(1) double bond is 1.259 (10) Å and C(6)–C(7) is 1.346 (10) Å, reflecting the reduction of the original acetylene triple bond to a double bond. The organic molecule is bonded via N(1) to Ru(2) by a donative bond of 2.190 (6) Å. N(2) bridges the metal–metal bond with Ru(1)–N(2) and Ru(2)–N(2) distances of 2.118 (6) and 2.166 (6) Å, respectively.

The nature of this latter bonding interaction is not trivial. C(6)–C(7) is a double bond, C(6) is bonded to H(61) and, furthermore, to both ruthenium atoms. This might suggest a 2e–3c interaction between the ethylene fragment and the two ruthenium atoms, but Ru(1)–C(6) is much longer that Ru(2)–C(6). Furthermore, regarding Ru(2) as a substituent, the substituents of the C(7)–C(6) moiety are not drastically distorted from the olefinic plane as is demonstrated by the Newman projection along this bond which is depicted in Figure 3.

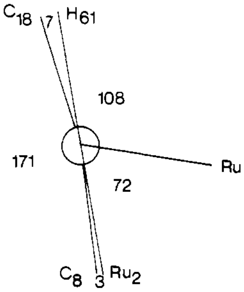

Figure 3. Newman projection along C(6)–C(7), including H(61).

Therefore, the bonding interaction between Ru(1) and C(6)=C(7) can best be regarded as weak η^2 bonding, resulting in a Ru(1)–C(6) distance of 2.273 (8) Å. In fact, the EAN rule requires the additional donation of two electrons from the organic ligand. In an analogous σ,η^2-bridging mode of ethylene fragments, Ru–C bonds of 2.332 (5) and 2.295 (5) Å have been reported[23] which are long but not as extreme as the bond distance of Ru(1)–C(7).

A fully analogous type of ethylene coordination has been observed in $W(CO)_4[W(CO)_5C_5H_8(CH_3)_3]$ with metal–carbon bond lengths of 2.26 (2) and 2.49 (2) Å for the η^2 coordination of the C=C double bond. These values compare very well with the values as obtained for $Ru_2(CO)_5$(AIB; *t*-Bu,-phenyl,H).[24]

IR. ν(CO) Stretching Region. All the complexes have characteristics ν(CO) absorption patterns. The IR spectra of the $Ru_2(CO)_5$(AIB) complexes (compounds II) exhibit four strong bands between 2100 and 1900 cm^{-1} due to the four terminal carbonyl groups and one band of medium intensity near 1830 cm^{-1} belonging to the bridging carbonyl group. The relative intensities and positions of the bands of all the Ru_2-

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(22) Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1–52.

(23) Sappa, E.; Manotti Lanfredi, A. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1979**, *36*, 197–203.

(24) Levisalles, J.; Rose-Munch, F.; Rudler, H.; Daran, J. C.; Dromzee, Y.; Jennin, Y. *J. Chem. Soc., Chem. Commun.* **1980**, 685–687.

Table VII. ^1H NMR Data (ppm Relative to Me_4Si; Solvent $CDCl_3$)

R,R′,R″	chemical shift, ppm	H_3	H_4	H_1[a]
	$Ru_2(CO)_5$(AIB; R,R′,R″) (II)			
t-Bu,phenyl,H (IIa)	1.07, 1.25 (*t*-Bu), 7.23 (Ph)	5.84	8.22	8.53
t-Bu,*p*-tol,H (IIb)	1.05, 1.27 (*t*-Bu), 2.12 (*p*-tol), 7.09, 7.39 (*p*-tol)[b]	5.84	8.21	8.42
t-Bu,*t*-Bu,H (IIc)	1.02, 1.23 (*t*-Bu), 1.18 (*t*-Bu)	5.46	8.18	7.89
t-Bu,mc,H (IIf)	0.98, 1.28 (*t*-Bu), 2.76 (mc)[c]	5.72	8.14	9.67
t-Bu,mc,mc (IId)	0.97, 1.33 (*t*-Bu), 3.17, 3.74 (mc)	5.66	8.14	
i-Pr,mc,mc (IIe)	0.84/0.95, 1.18/1.35 (*i*-Pr),[d] 2.39 (*i*-Pr),[e] 3.72, 3.72, 3.76 (mc)	5.31	8.08	
i-Pr,mc-d_3,mc-d_3[c]	0.84/0.95, 1.18/1.35 (*i*-Pr), 2.39, 3.83 (*i*-Pr)	5.31	8.08	
	$Ru_2(CO)_5$(AIB; R,R′,R″)(R‴C≡CR‴) (III)			
t-Bu,mc,mc[g] (IIIa)	1.13, 1.27 (*t*-Bu), 3.57, 3.66, 3.69, 3.80 (mc)	5.39	7.80	
i-Pr,mc,mc[g] (IIIb)	0.86/1.19, 1.25/1.32 (*i*-Pr), 2.62 (*i*-Pr),[e] 3.01, 3.74, 3.76, 3.87 (mc)	5.36	7.86	
c-Hx,mc,mc[g] (IIIc)	1–2 (c-Hx),[f] 3.62, 3.71, 3.74, 3.84 (mc)	5.38	7.80	
t-Bu,mc-d_3,mc-d_3[g] (IIIa′)	1.13, 1.27 (*t*-Bu), 3.69, 3.80 (mc)	5.39	7.80	
t-Bu,mc-$d_3$mc-d_3[h] (IIIa′)	1.13, 1.27 (*t*-Bu)	5.39	7.80	
i-Pr,mc,mc[h] (IIIb′)	0.86/1.19, 1.25/1.32 (*i*-Pr), 2.62 (*i*-Pr),[e] 3.74, 3.87 (mc)	5.36	7.86	
	$Ru_2(CO)_4$(AIB; R,R′,R″)(R‴C≡C_1R‴) (IV)			
t-Bu,mc,mc[g] (IVa)	1.23, 1.32 (*t*-Bu), 3.59, 3.66, 3.79, 3.82 (mc)	5.63	7.97	
t-Bu,mc,mc[h] (IVa′)	1.23, 1.32 (*t*-Bu), 3.66, 3.79 (mc)	5.63	7.97	
t-Bu,phenyl,H[g] (IVb)	0.99, 1.36 (*t*-Bu), 3.89, 3.96 (mc)	5.61	8.27	10.37

[a] J_{H_3,H_4} = 2 Hz; J_{H_3,H_1} = 0–1 Hz. [b] J_{AB} = 9 Hz. [c] mc = methoxycarbonyl; mc-d_3 = trideuteriomethoxycarbonyl. [d] Values separated by a slant correspond to diastereotopic pairs. [e] Septet; J = 7 Hz. [f] Broad multiplet. [g] R‴ = mc. [h] R‴ = mc-d_3.

$(CO)_5$(AIB) (II) complexes are comparable, indicating that the $Ru_2(CO)_5$–metal carbonyl fragments are similar to the one of $Ru_2(CO)_5$(AIB; *t*-Bu,phenyl,H) (compound IIa) which has been established by the X-ray structure.

The IR spectra of the $Ru_2(CO)_5$(AIB)(alkyne) complexes (compounds III) contain exclusively four strong bands between 2090 and 1970 cm^{-1} in the metal carbonyl stretching region. Accordingly, the $Ru_2(CO)_5$ units in these complexes contain five terminal carbonyl groups.

For the $Ru_2(CO)_4$(AIB)(alkyne) complexes (compounds III), three intense absorptions were observed between 2060 and 1980 cm^{-1} and one weak band near 1975 or 1955 cm^{-1}. This indicates that the $Ru_2(CO)_4$ units contain four terminal carbonyl groups. The IR data listed in Table VI include the ν(CO) frequencies of the methoxycarbonyl groups, if any present. These C=O vibrations appear near 1700 cm^{-1}.

^1H NMR Data. The ^1H NMR data of the complexes are listed in Table VII.

The $Ru_2(CO)_5$(AIB) complexes (compounds II) contain a buten-1-yl fragment. The resonances for the hydrogen atoms on the 4-positions of this fragment (H_4) are observed near 8.2 ppm, which is normal for an α-hydrogen relative to a =NR group.[25,26] The hydrogen atoms on the 3-positions of the butenyl skeletons appear in between 5.3 and 5.85 ppm, indicating that one of the C=N double bonds of the DAB building block in the ligand skeleton is reduced to a single bond. This is in agreement with the crystal structure of $Ru_2(CO)_5$(AIB; *t*-Bu,phenyl,H) (IIa), which established the single bond character of C(8)–N(2). The chemical shifts of the hydrogen atoms on the 1-position (H_1) are found in between 7.89 and 9.67 ppm and strongly depend upon the substituents on the 2-positions.

The crystal structure of $Ru_2(CO)_5$(AIB; *t*-Bu,phenyl,H) (IIa) indicated a very weak η^2-bond interaction between the C=C double bond of the butenyl fragment and Ru(1). The chemical shift values of H_1 in the $Ru_2(CO)_5$(AIB) complexes (compounds II) with phenyl, *p*-tolyl, or *tert*-butyl as a substituent attached to the 2-position of the AIB skeleton appear in the same regions as the hydrogen atoms of the σ-C,σ-C′-bonded acetylenes in $Ru_2(CO)_4(DAB)(\eta^2\text{-acetylene})$[27,28] (compounds V). This indicates that there is hardly any back-bonding to the weakly η^2-coordinating C=C double bond of the organic fragment.

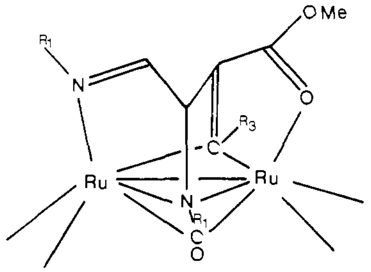

Figure 4. Proposed structure of $Ru_2(CO)_5$(AIB) complexes containing methoxycarbonyl groups on the 2-positions. (Key for complexes: for IId R_1 = *t*-Bu, R_2 = R_3 = $COOCH_3$; for IIe R_1 = *i*-Pr, R_2 = R_3 = $COOCH_3$; for IIf R_1 = *t*-Bu, R_2 = $COOCH_3$, R_3 = H. For other codes see Figure 9.)

The chemical shift of 9.67 ppm for H_1 in $Ru_2(CO)_5$(AIB; *t*-Bu,CH_3O_2C,H) (IIf) is approximately 1.4-ppm downfield as compared with the chemical shifts of H_1 in the other $Ru_2(CO)_5$(AIB) complexes (compounds II). This extreme low-field shift is in distagreement with η^2 coordination of the C=C double bond in the ligand, and we therefore suggest that in this complex the 1-buten-1-yl is coordinated to both ruthenium atoms via a 2e–3c interaction. So that the EAN rule can be satisfied in these complexes, the carbonyl group should be coordinated to Ru(1) via an oxygen lone pair. The proposed structure is depicted in Figure 4. Since this type of coordination is sterically favored above the η^2-C=C coordination, it is assumed that all the $Ru_2(CO)_5$(AIB) complexes containing methoxycarbonyl groups (IId–f) satisfy the 18e rule by coordination of the carboxylato group on the 2-position.

Interestingly, long-range coupling of nearly 1 Hz can be observed between H_3 and H_1. Therefore, since H_3 is also coupled with H_4 (J = 2 Hz), the resonance pattern of H_3 is a doublet of doublets.

Due to the fact that the AIB ligands consist of a DAB ligand and an alkyne, the imine and amine moieties have the same substituents. These substituents, however, are anisochronous.

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(25) Staal, L. H.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1979**, *175*, 73–86.

(26) tom Dieck, H.; Renk, I. W.; Franz, K. D. *J. Organomet. Chem.* **1975**, *94*, 417–424.

(27) Staal, L. H.; Polm, L. H.; Vrieze, K.; Ploeger, F.; Stam, C. H. *J. Organomet. Chem.* **1980**, *199*, C13–C16.

(28) Staal, L. H.; van Koten, G.; Vrieze, K.; Ploeger, F.; Stam, C. H., *Inorg. Chem.* **1981**, *20*, 1830–1835.

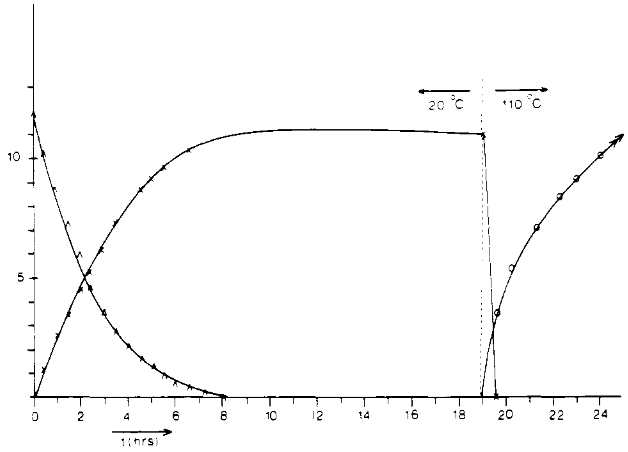

Figure 5. Plot of the conversion of $Ru_2(CO)_5$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$) in the reaction mixture for the catalytic conversion of dimethyl acetylenedicarboxylate into hexakis(methoxycarbonyl)benzene: Λ = $Ru_2(CO)_5$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C); × = $Ru_2(CO)_5$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$); ○ = hexakis(methoxycarbonyl)benzene. *y* axis is arbitrary units based upon the area underneath the high-pressure liquid chromatography peaks.

In $Ru_2(CO)_5$(AIB; *i*-Pr,CH_3O_2C,CH_3O_2C] (IIe), the septet of the isopropyl substituent attached to the amine moiety is obscured by the signals of the methylcarboxylato groups. This complex has therefore also been prepared with deuterated carboxylato groups, thus allowing us to locate this septet at 3.83 ppm.

The resonance pattern of the AIB ligands in $Ru_2(CO)_5$(AIB)(alkyne) (compounds III) is comparable with the resonance pattern of the $Ru_2(CO)_5$(AIB) complexes (compounds II). However, two additional singlets are observed for the methoxycarbonyl groups of the alkyne. Assignment of the singlets near 3.8 ppm to the methoxycarbonyl groups on either the AIB ligand or the alkyne is possible due to the preparation of complexes containing two deuterated methoxycarbonyls. For $Ru_2(CO)_5$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$) (IIIa), the signals at 3.57 and 3.66 ppm belong to the methoxycarbonyl groups on the AIB ligand and the signals at 3.69 and 3.80 ppm to the methoxycarbonyl groups on the alkyne. For $Ru_2(CO)_5$(AIB; *i*-Pr,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$) (IIIb), the signals at 3.61 and 2.76 belong to the alkyne and the signals at 3.74 and 3.87 to the AIB ligand.

The $Ru_2(CO)_4$(AIB)(alkyne) complexes (compounds IV) give resonance patterns which are comparable with those of the $Ru_2(CO)_5$(AIB)(alkyne) complexes (III). The four singlets of the methoxy groups of $Ru_2(CO)_4$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$) (IVa) can be assigned due to the preparation of the complex containing deuterated dimethyl acetylenedicarboxylate. The singlets at 3.66 and 3.79 ppm belong to the methoxycarbonyl groups on the 1- and 2-positions of the AIB ligand, while the signals at 3.5. and 3.82 ppm belong to the coordinated dimethyl acetylenedicarboxylate.

The chemical shift value of 10.37 ppm for H_1 in $Ru_2(CO)_4$(AIB; *t*-Bu,phenyl,H)($CH_3O_2CC{\equiv}CCO_2CH_3$) (IVb) is extremely downfield and indicates that the C=C double bond of the butenyl fragment is not coordinated to either of the ruthenium atoms. We therefore propose that this fragment is bonded to both ruthenium atoms via a 2e–3c bond.

The proposed structures for $Ru_2(CO)_4$(AIB)(alkyne) (IV) and $Ru_2(CO)_5$(AIB)(alkyne) (III) are shown as part of a reaction sequence in Figure 9.

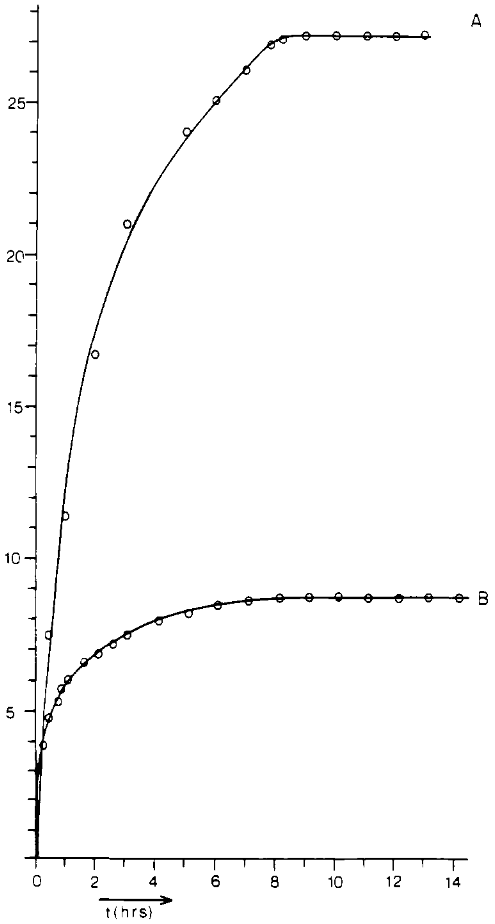

Figure 6. Plot of hexakis(methoxycarbonyl)benzene production against time with use of (A) 0.9 mg of $Ru_2(CO)_5$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$) and (B) 6.5 mg of $Ru_2(CO)_5$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$). *y* axis is in arbitrary units.

Catalytic Alkyne Cyclotrimerization. $Ru_2(CO)_6$(DAB) (I), $Ru_2(CO)_5$(AIB) (II), $Ru_2(CO)_5$(ABI)(alkyne) (III), and $Ru_2(CO)_4$(AIB)(alkyne) (IV) complexes exhibit catalytic activity toward the cyclotrimerization of alkynes. The reactions have been studied by means of high-pressure liquid chromatography for the trimerization of dimethyl acetylenecarboxylate (see Table II).

In Figure 5, the relative concentrations of $Ru_2(CO)_5$(AIB) (II) and subsequent products are plotted against time for a standard reaction mixture (molar ratio for complex vs. dimethyl acetylenedicarboxylate is 1:400). At room temperature $Ru_2(CO)_5$(AIB) (II) reacts with the alkyne, forming $Ru_2(CO)_5$(AIB)(alkyne) (IV) while hexakis(methoxycarbonyl)benzene has not yet been formed. Several experiments with various temperatures showed that the cyclotrimerization does not occur when the reaction temperature is below 100 °C. In Figure 5 is shown that raising the temperature up to 110 °C leads to a rapid conversion of $Ru_2(CO)_5$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$) (IIIa) into a subsequent product which could not be separated under the conditions employed for the high-pressure liquid chromatography. Simultaneously, the catalytic cyclotrimerization starts.

In Figure 6, two plots of hexakis(methoxycarbonyl)benzene production are shown. In curve A, 0.9 mg of $Ru_2(CO)_4$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$) (IVa) has been used to show that this compound can also be used as a catalyst. The number of catalytic cycles for this complex is 380. In curve B, 6.5 mg of $Ru_2(CO)_5$(AIB; *t*-Bu,CH_3O_2C,CH_3O_2C)($CH_3O_2CC{\equiv}CCO_2CH_3$) (IVa) has been used to catalyze the trimerization of 0.57 g of $CH_3O_2CC{\equiv}CCO_2CH_3$. After 8 h of reaction, all the acetylene has been converted into hexakis(methoxycarbonyl)benzene.

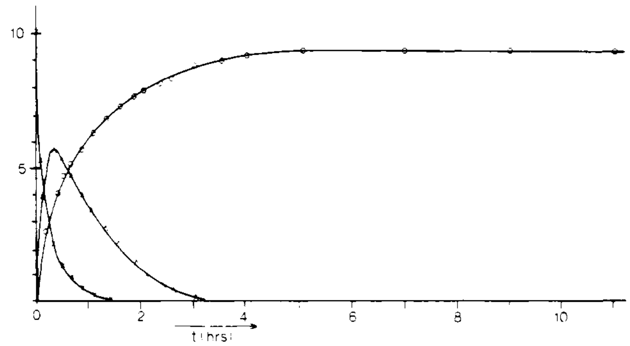

Figure 7. Plot of the conversion of $Ru_2(CO)_5$(AIB; *t*-Bu,phenyl,H) (indicated by ×) into $Ru_2(CO)_5$(AIB; *t*-Bu,phenyl,H)($CH_3O_2CC{\equiv}CCO_2CH_3$) (indicated by Λ) during the formation of hexakis(methoxycarbonyl)benzene (indicated by O). *y* axis is in arbitrary units.

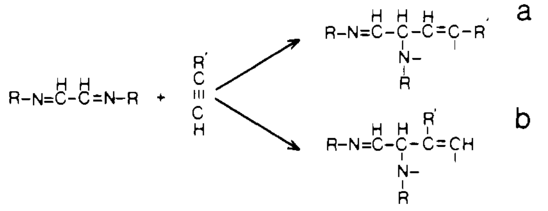

Figure 8. Two possible isomers after C–C bond formation between DAB and a monosubstituted alkyne.

$Ru_2(CO)_5$(AIB; *t*-Bu,phenyl,H) (IIa) can also be used to trimerize dimethyl acetylenedicarboxylate as is shown in the product vs time plot which is depicted in Figure 7. The conversion of $Ru_2(CO)_5$(AIB; *t*-Bu,phenyl,H) (IIa) is completed in 1.5 h of reaction time. The formation of $Ru_2(CO)_5$(AIB; *t*-Bu,phenyl,H)($CH_3O_2CC{\equiv}CCO_2CH_3$) (IVb) can be detected, but this product is thermally unstable. Interestingly, the termination of trimerization reaction coincides with the total conversion of $Ru_2(CO)_5$(AIB; *t*-Bu,phenyl,H) (IIa).

In an analogous manner, methyl acetylenecarboxylate can be trimerized into 1,3,5-tris(methoxycarbonyl)benzene. This reaction produces regiospecifically the 1,3,5-substituted benzene, as was concluded from the ^1H NMR spectra.

When $Ru_2(CO)_6$(DAB) (I) is reacted with $HC{\equiv}CH$, benzene is formed in approximately equimolar ratio with $Ru_2(CO)_4$(DAB)($HC{\equiv}CH$) (V). This latter complex, however, does not exhibit catalytic activity when reacted with acetylene.

Discussion

Complex Formation. The complexes are formed in a reaction sequence which starts with the reaction between $Ru_2(CO)_6$(DAB) (I) and an alkyne ligand (Figure 9, I). In $Ru_2(CO)_6$(DAB) (I) one of the C=N double bonds is η^2-coordinated, resulting in an activation of the imine moiety toward C–C bond formation. The coupling reaction may be considered as an insertion of the acetylene into the formal Ru–C bond between the DAB ligand and the $Ru_2(CO)_6$ unit. When monosubstituted alkynes are used, the reaction occurs with 100% regioselectivity. Thus of the two possible isomers which are shown in Figure 8 only isomer b is formed.

$Ru_2(CO)_5$(AIB) (II) complexes (Figure 9, II) react with alkynes to form $Ru_2(CO)_5$(AIB)(alkyne) (III) complexes. Some information concerning the structure of the complexes was obtained from the IR spectra, showing that the bridging carbonyl group changed into a terminal CO group. Therefore, these complexes contain a $Ru(CO)_2$ and a $Ru(CO)_3$ fragment. The alkyne will coordinate via the π electrons as a 2e donor to the $Ru(CO)_2$ fragment, but no conclusion can be drawn concerning the position of the $Ru(CO)_2$ and $Ru(CO)_3$ fragments relative to the AIB ligand on the basis of the spectroscopic results. Purely on steric grounds, the structure shown in Figure 9 (III) is proposed.

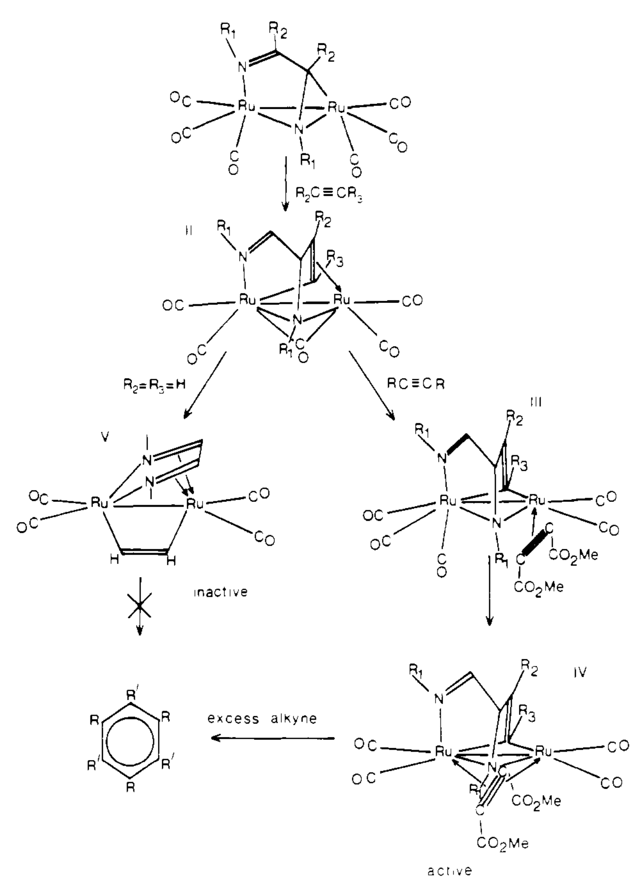

Figure 9. Reaction sequence for the reaction between $Ru_2(CO)_6$(DAB) (I) and alkynes. Key for complexes: Ia, R_1 = *t*-Bu; Ib, R_1 = *i*-Pr; Ic, R_1 = c-Hx; IIa, R_1 = *t*-Bu, R_2 = phenyl, R_3 = H; IIb, R_1 = *t*-Bu, R_2 = *p*-tol, R_3 = H; IIc, R_1 = *t*-Bu, R_2 = *t*-Bu, R_3 = H; IIIa, R_1 = *t*-Bu, R_2 = R_3 = $COOCH_3$; IIIb, R_1 = *i*-Pr, R_2 = R_3 = COOMe; IIIc, R_1 = c-Hx, R_2 = R_3 = $COOCH_3$; IVa, R_1 = *t*-Bu, R_2 = R_3 = COOMe; IVb, R_1 = *t*-Bu, R_2 = phenyl, R_3 = H. See Figure 4 for explanation for IId–f.

$Ru_2(CO)_5$(AIB)(alkyne) (III) complexes lose a carbonyl group after heating. The reaction products, $Ru_2(CO)_4$(AIB)(alkyne), contain an alkyne ligand that on the basis of electron counting should act as a 4e donor bridging the $Ru_2(CO)_4$ unit. The proposed structure is shown in Figure 9 (IV).

When the acetylene ($HC{\equiv}CH$) is used as an alkyne, a side reaction can be observed; $Ru_2(CO)_4$(DAB)(μ-$HC{\equiv}CH$) (V) complexes are formed which are shown in Figure 9 (V). The structure of these complexes has recently been established by a single-crystal X-ray structure.[27,28] The carbon–carbon bond formation and the subsequent selective cleavage of this bond is analogous to the reaction pathway of $Ru_2(CO)_6$(DAB) with uncoordinated DAB ligands. In these reactions a C–C bond is formed between two DAB ligands, resulting in the formation of $Ru_2(CO)_5$(IAE) and $Ru_2(CO)_4$(IAE) [IAE = bis[(alkylimino)(alkylamino)ethane]]. After prolonged heating, $Ru_2(CO)_4(DAB)_2$ complexes are formed in which the newly formed C–C bond has selectively been broken,[1] resulting in two σ-N,μ^2-N′,η^2-C=N′-coordinated DAB ligands.

Catalytic Cyclotrimerization Reaction. In order to obtain information about the possible involvement of the coordinated acetylenes in the complexes which have been used as catalyst for the trimerization reaction, we have used complexes containing deuterated methyl carboxylate groups. The trimerization of dimethyl acetylenedicarboxylate with $Ru_2(CO)_5$(AIB;

$t\text{-}\mathrm{Bu,CD_3O_2C,CD_3O_2C)(CD_3O_2CC{\equiv}CCO_2CD_3)}$ (IId) produces 100% nondeuterated hexakis(methoxycarbonyl)benzene (detected with EI MS and FD MS). This result in addition to the results of the high-pressure liquid chromatography experiments is evidence that neither of the complexes described above are catalysts. In fact, the catalyst is produced in a step following the $\mathrm{Ru_2(CO)_4(AIB)(alkyne)}$ (IV) formation.

In the literature, extensive information is available about the catalytic cyclotrimerization of alkynes using alkyne complexes.[29–34] The mechanism which is at present best understood is the formation of a metallocyclopentadiene out of two acetylenes followed by reaction with a third acetylene resulting in benzene formation. The metallocyclopentadiene intermediates have been isolated for a variety of metal complexes.[8,35–46] Stone et al. succeeded in the isolation of metallocycloheptatriene systems with Ni and Pt complexes starting from $\mathrm{F_3CC{\equiv}CCF_3}$. These types of complexes can be envisaged as a subsequent intermediate in the benzene formation.[47] Green et al. reported the formation of a rutheniocycloheptatriene which converted into a η^2-coordinated benzene, showing that the metallocycle is indeed an intermediate.[48]

In contrast to the mononuclear catalysts, little is known about the benzene formation on multicenter catalysts. A well-established example is $\mathrm{Co_2(CO)_4}(t\text{-}\mathrm{Bu\text{-}C{=}CHCH{=}CHCH{=}C}\text{-}t\text{-}\mathrm{Bu})$ in which three coupled acetylenes act as two π-allyl ligands with respect to the $\mathrm{Co_2(CO)_4}$ unit.[49] Furthermore, $\mathrm{Fe_2(CO)_6(dienyl)}$ complexes are known, containing η^4-coordinated metallocyclopentadiene fragments. These complexes are also catalysts for the cyclotrimerization of alkynes.[32]

According to the literature data, catalytic cyclotrimerization of alkynes using binuclear complexes as a catalyst is possible. Therefore, the actual catalyst formed out of $\mathrm{Ru_2(CO)_5(AIB)}$ (II) with excess of alkynes might be a subsequent binuclear product, but there is no direct evidence that the catalyst is not a mononuclear decomposition product.

The exclusive formation of 1,3,5-tris(methoxycarbonyl)benzene is a very uncommon feature in the catalytic alkyne trimerization.[29] This in addition to the promising turnover numbers makes $\mathrm{Ru_2(CO)_6(DAB)}$ complexes valuable starting materials for the formation of the active catalyst.

Conclusions

The C–C bond formation between the η^2-C=N-coordinated imine moiety in $\mathrm{Ru_2(CO)_6(DAB)}$ and a variety of alkynes is additional evidence for the activation of the C=N double bonds due to η^2 coordination. Earlier examples were the IAE formation in ruthenium[1] and molybdenum[2] complexes. It may therefore be concluded that the carbon–carbon bond formation is a more general behavior of these activated DAB systems.[1]

$\mathrm{Ru_2(CO)_6(DAB)}$ complexes produce active catalysts for the cyclotrimerization of alkynes. Since $\mathrm{Fe_2(CO)_6(DAB)}$,[2] $\mathrm{FeRu(CO)_6(DAB)}$,[50] $\mathrm{Os_2(CO)_6(DAB)}$,[5] $\mathrm{MnCo(CO)_6(DAB)}$,[6] and $\mathrm{ReCo(CO)_6(DAB)}$[6] are electronically and sterically related to $\mathrm{Ru_2(CO)_6(DAB)}$, attention has to be paid to the possible catalytic activity of these complexes. It has indeed been found that $\mathrm{Fe_2(CO)_6(DAB)}$ reacts with alkynes under mild conditions to form $\mathrm{Fe_2(CO)_4(alkyne)_2(DAB)}$.[51]

Further investigations are required in order to obtain insight in the mechanism of the cyclotrimerization of alkynes using $\mathrm{Ru_2(CO)_6(DAB)}$ derivatives as a catalyst.

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Registry No. Ia, 74552-68-4; Ib, 74552-69-5; Ic, 74552-70-8; IIa, 78199-19-6; IIb, 78199-20-9; IIc, 78199-21-0; IId, 78199-22-1; IIe, 78199-23-2; IIf, 78199-24-3; IIIa, 78199-34-5; IIIb, 78231-82-0; IIIc, 78199-33-4; IVa, 78199-35-6; IVb, 78217-08-0; $\mathrm{C_6H_5C{\equiv}CH}$, 536-74-3; $\mathrm{CH_3}\text{-}p\text{-}\mathrm{C_6H_4C{\equiv}CH}$, 766-97-2; $t\text{-}\mathrm{BuC{\equiv}CH}$, 917-92-0; $\mathrm{CH_3O_2CC{\equiv}CCO_2CH_3}$, 762-42-5; $\mathrm{CH_3O_2CC{\equiv}CH}$, 922-67-8; $\mathrm{(CH_3O_2C)_6C_6}$, 6237-59-8; $\mathrm{(CH_3O_2C)_3C_6H_3}$, 2672-57-3.

Supplementary Material Available: Tables of elemental analyses, temperature factors, and structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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(29) Bird, C. W. "Transition Metal Intermediates in Organic Synthesis"; Academic Press: New York, 1967.

(30) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1–8.

(31) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245.

(32) Hübel, W.; Hoogzand, C. *Chem. Ber.* **1960**, *93*, 103–109.

(33) Meriwether, L. S.; Leto, M. F.; Colthup, E. C.; Kennerly, G. W. *J. Org. Chem.* **1962**, *27*, 3930–3941.

(34) Tobe, M. L. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. Two* **1974**, *9*, 271.

(35) Mays, M. J. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *6*, 227.

(36) Collman, J. P.; Kang, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 844–851.

(37) Bunker, M. J.; Green, M. L. H.; Couldwell, C.; Prout, K. *J. Organomet. Chem.* **198/**, *192*, C6–C8.

(38) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157–167.

(39) Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1970**, *21*, 431–443.

(40) Blomquist, A. T.; Maitlis, P. M. *J. Am. Chem. Soc.* **1962**, *84*, 2329–2334.

(41) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93–99.

(42) Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1967**, *7*, P22–P23.

(43) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666–1668.

(44) Bruce, M. I.; Gardner, R. C. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1979**, 906–913.

(45) Itoh, J. *Fundam. Res. Homogeneous Catal.* **1979**, *3*.

(46) Bowden, F. L.; Lever, A. B. P. *Organomet. Chem. Rev.* **1968**, *3*, 227–279.

(47) Browning, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 97–101.

(48) Burt, R.; Cooke, M.; Green, M. *J. Chem. Soc. A* **1970**, 2981–2986.

(49) Mills, O. S.; Robinson, G. *Proc. Chem. Soc., London* **1964**, 187.

(50) Staal, L. H.; Polm, L. H.; van Koten, G.; Vrieze, K. *Inorg. Chim. Acta* **1979**, *37*, L485–L487.

(51) Staal, L. H.; Vrieze, K., unpublished results.