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Metal–Metal Bond Fission and Formation and C–C Couplings in Reactions of Diruthenium 1,4-Diaza-1,3-butadiene Complexes with Alkynes[1]

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$Ru_2(CO)_6$(*t*-Bu-DAB) (1), with a σ-N, μ_2-N′, η^2-C=N′ 6e bridging *t*-Bu-DAB [= *t*-BuN=CHCH=N-*t*-Bu] ligand, reacts with various alkynes RC≡CR′ [R = Ph, C(O)OMe, R′ = H; R = R′ = C(O)OMe, CF_3] to give in high yield $Ru_2(CO)_6$[*t*-BuN=CHCN(N-*t*-Bu)CR=CR′] (2). The proposed mechanism for their formation comprises a direct electrophilic attack of the alkyne on the η^2-C=N coordinated imine moiety, resulting in the observed C–C bond formation. The X-ray single crystal structure of **2a** with R = R′ = CF_3 has been established. Orange crystals of **2a** ($Ru_2C_{20}H_{20}N_2O_6F_6$, mol wt 700.52, $Z = 4$) are monoclinic, space group $P2_1/n$, and have cell constants $a = 17.475$ (4) Å, $b = 10.446$ (2) Å, $c = 13.742$ (3) Å, and $\beta = 96.05$ (2)°. A total of 3359 reflections (Mo Kα, $\mu = 12.68$ cm^{-1}) were used in the refinement which converged to a final R value of 0.048 ($R_w = 0.091$). The molecular structure consists of two $Ru(CO)_3$ fragments [nonbonding Ru⋯Ru distance = 3.359 (4) Å; all CO ligands are terminally bonded] which are bridged by an organic ligand resulting from C–C coupling of the η^2-C=N coordinated imine C atom of **1** with one of the alkyne C atoms. The other alkyne C atom becomes σ-bonded to the Ru center to which both N atoms are bonded. Furthermore, the reduced alkyne bond is η^2-C=C coordinated to the second Ru center. Complexes **2** easily and reversibly lose one CO ligand to give $Ru_2(CO)_5$[*t*-BuN=CHCH(N-*t*-Bu)CR=CR′] (**3**), of which the crystal structure of **3d** (R = Ph, R′ = H) has been published previously. In **3** the Ru–Ru bond is restored and one of the CO ligands is now bridging the metals. The bridging CO ligand can be substituted by a MeOC(O)C≡CC(O)OMe molecule to give $Ru_2(CO)_4$[*t*-BuN=CHCH(N-*t*-Bu)CR=CR′](μ_2-MeOC(O)C≡CC(O)OMe) (4). Complexes **3** can also react with a second alkyne to give $Ru_2(CO)_5$[*t*-BuN=CHCH(N-*t*-Bu)$C_4R_2R'_2$] (**5**) via the C–C coupling of this alkyne to the C atom of the first alkyne that is already σ-bonded to Ru in **2**. In this way also mixed products involving the subsequent coupling of two different alkynes could be synthesized. The X-ray single crystal structure of **5a** (R = R′ = C(O)OMe) has been determined. Yellow crystals of **5a** ($Ru_2C_{27}H_{26}N_2O_{13}$, mol wt 794.69, $Z = 8$) are monoclinic, space group $P2_1/n$, and have cell constants $a = 19.694$ (4) Å, $b = 18.629$ (3) Å, $c = 18.851$ (2) Å, and $\beta = 110.378$ (14)°. A total of 3499 reflections (Mo Kα, $\mu = 9.89$ cm^{-1}) were used in the refinement which converged to a final R value of 0.052 ($R_w = 0.080$). The molecular structure consists of a $Ru(CO)_2$ and a $Ru(CO)_3$ fragment [nonbonding Ru⋯Ru distance = 3.3059 (19) Å; all CO ligands are terminally bonded]. The C atoms of the second alkyne bond with the C atom of the first alkyne to which it is coupled to an allyl group η^3-bonded to the Ru to which both N atoms are coordinated and σ-bonded to the second Ru center. The reaction sequence **1** → **2** → **3** → **5** involves a unique Ru–Ru bond fission–formation–fission sequence. The subsequent C–C couplings are analogous to the known sequential linking of alkynes on dinuclear Mo and Cr complexes. The activation of the η^2-C=N bonded imine moiety and the flexible nature of the Ru–Ru interaction are crucial factors for the observed C–C coupling reactions to take place.

Introduction

In the past decade in our laboratory much attention has been devoted to the coordination chemistry of α-diimine ligands in transition-metal complexes.[3] The availability of two N lone pairs and two C=N π-bonds for coordination to one or more metal centers leads to a number of different bonding modes in mono-, di-, and polynuclear metal complexes. Until now metal–metal bonded dinuclear complexes have been found with the α-diimine bonded as a σ,σ-N,N′ chelating 4e donor,[4] a σ-N, μ_2-N′, η^2-C=N′ bridging 6e donor,[5] or a σ,σ-N,N′, η^2,η^2-C=N,C=N′ bridging 8e donor.[6] Also the reactivity of the formed α-diimine complexes toward various organic substrates has been studied and has resulted in a number of C–C, C–N, C–H, and N–H coupling reactions.[3] The reactivity of the dinuclear complexes with a σ-N, μ_2-N′, η^2-C=N′ bridging α-diimine ligand appears to be largely determined by the nature of the η^2-C=NM interaction.

In the reactions of $Ru_2(CO)_6$(R-DAB) (1) (R-DAB = RN=CHCH=NR; R = *i*-Pr, c-Hex, *t*-Bu) with alkynes this activation leads to C–C coupling reactions of the

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Table I. IR and FI-Mass Data and Elemental Analyses of $Ru_2(CO)_6$[AIB(*t*-Bu,R,R′)] (2a, R = R′ = CF_3; 2b, R = R′ = C(O)OMe; 2c, R = C(O)OMe, R′ = H; 2d, R = Ph, R′ = H), $Ru_2(CO)_5$[AIB(*t*-Bu,R,R′)] (3a, R = R′ = CF_3), and $Ru_2(CO)_5$[*t*-BuN=CHCH(N-*t*-Bu)$C_4R_2R'_2$] (5b, R = CF_3, R′ = C(O)OMe; 5c, R = H, R′ = C(O)OMe)

compd	IR (ν_s(C=O),[a] cm^{-1}	FI-mass (calcd)[b]	elemental anal. obsd (calcd) C	H	N
2a	2101 (s), 2054 (vs), 2024 (s), 1981 (s), 1972 (s) [CH_2Cl_2]	701 (700.52)	34.17 (34.29) F: 16.75 (16.27)	2.93 (2.88)	4.00 (4.00)
2b	2085 (s), 2032 (vs), 2014 (s), 1974 (s), 1964 (m), 1724 (m), 1693 (m) [CH_2Cl_2]	681 (680.59)	38.99 (38.82)	3.97 (3.85)	4.24 (4.12)
2c	2083 (s), 2057 (s), 2009 (vs), 1995 (s), 1984 (s), 1723 (m) [hexane]	594[c] (622.55)	41.03 (40.71)	4.21 (4.16)	3.98 (4.13)
2d	2077 (s), 2050 (s), 1998 (s, b) 1975 (sh) [CH_2Cl_2]	612[c] (640.61)	not analyzed		
3a	2051 (s), 2015 (vs), 1995 (m), 1950 (s), 1832 (m) [CH_2Cl_2]	673 (672.51)	34.02 (33.93)	2.94 (3.00)	4.13 (4.17)
5b	2080 (m), 2065 (vs), 2020 (vs), 1985 (m), 1715 (s) [CH_2Cl_2]	815 (814.62)	not analyzed		
5c	2081 (m), 2013 (vs), 1999 (m), 1944 (s), 1670 (m) [CH_2Cl_2]	678 (678.61)	not analyzed		

[a] Solvents in square brackets. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak. [b] Based on ^{101}Ru. [c] M^+ minus CO.

alkyne with the coordinated imine C atom. A number of such reactions with phenylacetylene, *p*-tolylacetylene, *tert*-butylacetylene, methyl propynoate, and dimethyl acetylenedicarboxylate have been reported from our laboratory several years ago.[7] These reactions resultes in the formation of products of the general formula $Ru_2(CO)_5$[AIB(R,R′,R″)].[8a] For R′ = R″ = C(O)OMe it was found that this product reacted further with a second equivalent of dimethyl acetylenedicarboxylate to give $Ru_2(CO)_5$[AIB(R,C(O)OMe,C(O)OMe)](μ_2-dimethyl acetylenedicarboxylate) which could be converted thermally into $Ru_2(CO)_4$[AIB(R,C(O)OMe,C(O)OMe)](μ_2-dimethyl acetylenedicarboxylate). Finally, when $Ru_2(CO)_6$(R-DAB) was reacted at higher temperatures with an excess of dimethyl acetylenedicarboxylate or methyl propynoate, a catalytic cyclotrimerization process was observed.[7,8b]

In this paper we report a more detailed study of the formation and structural features of the complexes reported in a previous paper on the reactions of 1 with alkynes.[7] It appeared that the formation of the $Ru_2(CO)_5$[AIB(R,R′,R″)] complexes reported previously was preceded by complexes of the type $Ru_2(CO)_6$[AIB(R,R′,R″)] (2), of which the X-ray crystal structure for R = *t*-Bu and R′ = R″ = CF_3 is included in this paper. The X-ray crystal structure determination of the complex with the previously proposed structure $Ru_2(CO)_5$[AIB(R,C(O)OMe,C(O)OMe)](μ_2-dimethyl acetylenedicarboxylate) showed that the structural assignment based on IR and ^1H NMR data was incorrect. Further, the complex $Ru_2(CO)_4$[AIB(R,C(O)OMe,C(O)OMe)](μ_2-dimethyl acetylenedicarboxylate) appeared not to be formed from the corresponding pentacarbonyl complex, as was initially assumed, but results from a different reaction pathway. The preparation and characterization with IR and ^1H, ^{13}C, and ^{19}F NMR spectroscopy of the AIB complexes and their derivatives are reported.

Table II. ^1H and ^{19}F NMR Data of $Ru_2(CO)_6$[AIB(*t*-Bu,R,R′)] (2a, R = R′ = CF_3; 2b, R = R′ = C(O)OMe; 2c, R = C(O)OMe, R′ = H; 2d, R = Ph, R′ = H), $Ru_2(CO)_5$[AIB(*t*-Bu,R,R′)] (3a, R = R′ = CF_3; 3b, R = R′ = C(O)OMe; 3c, R = C(O)OMe; R′ = H; 3d, R = PPh, R′ = H), $Ru_2(CO)_5$[AIB(*t*-Bu,R,R′)](μ_2-dimethyl acetylenedicarboxylate) (4a, R = R′ = C(O)OMe; 4b, R = Ph, R′ = H), and $Ru_2(CO)_5$[*t*-BuN=CHCH(N-*t*-Bu)$C_4R_2R'_2$] (5a, R = R′ = C(O)OMe; 5b, R = CF_3, R′ = C(O)OMe; 5c, R = H, R′ = C(O)OMe)[a]

	t-Bu	N=CH	N—CH	alkyne
2a	0.95, 1.41	8.11	5.03	^{19}F: −52.68, −46.26 (q, q, $^5J_{F,F}$ = 10.9 Hz)
2b	1.03, 1.09	7.12[b]	5.18[b]	3.66, 3.72 (s, s; OMe)
2c	1.06, 1.11	7.06[b]	5.18[b]	3.72 (s, OMe); 8.91 (s, =CH)
2d	1.11, 1.31	7.21[c]	5.55[d]	7.1–7.5 (m, Ph), 8.52 (d, *J* = 0.8 Hz; =CH)
3a	1.09, 1.13	8.24	5.57	^{19}F: −53.54, −55.88 (q, q, $^5J_{F,F}$ = 12.2 Hz)
3b[f]	0.97, 1.33	8.14	5.66	3.17, 3.74 (s, s; OMe)
3c[f]	0.98, 1.28	8.14	5.72	2.76 (s, OMe); 9.76 (s, =CH)
3d[f]	1.07, 1.25	8.22	5.84	7.23 (m, Ph), 8.53 (d, *J* = 0.8 Hz; =CH)
4a[f]	1.23, 1.32	7.97	5.63	3.59, 3.66, 3.79, 3.82 (4 × s, OMe)
4b[f]	0.99, 1.36	8.27	5.61	3.89, 3.96 (s, s, OMe; 10.37 (=CH)
5a[f]	1.13, 1.27	7.80	5.39	3.57, 3.66, 3.69, 3.80 (4 × s, OMe)
5b	1.23, 1.33	8.01	5.63	3.61, 3.85 (s, s, OMe) ^{19}F: −55.74, −54.92 (q, q, $^5J_{F,F}$ = 12.4 Hz)
5c	1.13, 1.34	7.60[e]	5.50[e]	3.66, 3.85 (s, s, OMe) 4.35, 6.42 (d, d, 2 Hz; =CH)

[a] ^1H NMR values in ppm relative to Me_4Si, measured in $CDCl_3$ solution, 293 K, spectrometer frequency (SF) = 100 MHz, ^{19}F NMR values in ppm relative to $CFCl_3$, measured in $CDCl_3$ solution, 293 K, SF = 94.2 MHz. [b] d, d; *J* = 7 Hz. [c] d, *J* = 8 Hz. [d] dd, *J* = 8 Hz/0.8 Hz. [e] d, d; *J* = 5 Hz. [f] Reported previously.[7]

Experimental Section

Materials and Apparatus. ^1H and ^{19}F NMR spectra were recorded on a Bruker AC100 spectrometer. The ^{13}C NMR spectra were obtained on Bruker WP80, AC100, and WM250 machines. IR spectra were measured with a Perkin-Elmer 283 spectrometer. The Field ionization (FI) mass spectra were obtained with a Varian MAT711 double-focussing mass spectrometer with a combined EI/FI/FD source. The samples were dissolved in dichloromethane and introduced via the direct insertion probe into the ion source, of which the temperature was generally selected in the range of 60–160 °C. Elemental analyses were carried out by the section Elemental Analysis of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

All preparations were carried out in an atmosphere of purified nitrogen, using carefully dried solvents. All column chromatography was performed by using silica gel (60 mesh, dried and activated before use) as the stationary phase. $Ru_2(CO)_6$(*t*-Bu-DAB),[9] $Ru_2(CO)_5$[*t*-BuN=CHCH(N-*t*-Bu)C_4(C(O)OMe)$_4$] (**5a**), $Ru_2(CO)_4$[AIB(*t*-Bu,C(O)OMe,C(O)OMe)](μ_2-dimethyl acetylenedicarboxylate) (**4a**), and $Ru_2(CO)_4$[AIB(*t*-Bu,Ph,H)](μ_2-dimethyl acetylenedicarboxylate) (**4b**) were prepared according to known procedures.[7] Phenylacetylene, methyl propynoate, and dimethyl acetylenedicarboxylate we distilled prior to use. Hexafluorobutyne was used as commercially obtained. The products

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[8] (a) AIB(R,R′,R″) is the abbreviation for the organic ligand resulting from the C–C bond formation between an R-DAB ligand and an alkyne R′C≡CR″. The backbone of the ligand is RN=C(H)C(H)(NR)C(R′)=CR″, which is 3-amino-4-imino-1-butene. (b) These cyclotrimerization reactions will be subject of a future publication.

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Table III. ^{13}C NMR Data of $Ru_2(CO)_6[AIB(t\text{-}Bu,R,R')]$ (2a, R = R′ = CF_3; 2b, R = R′ = C(O)OMe; 2c, R = C(O)OMe; R′ = H; 2d, R = Ph, R′ = H), $Ru_2(CO)_5[AIB(t\text{-}Bu,R,R')]$ (3a, R = R′ = CF_3; 3b, R = R′ = C(O)OMe; 3c, R = C(O)OMe, R′ = H; 3d, R = Ph, R′ = H), $Ru_2(CO)_4[AIB(t\text{-}Bu,R,R')][\mu_2$-dimethyl acetylenedicarboxylate) (4a, R = R′ = C(O)OMe; 4b, R = Ph, R′ = H), and $Ru_2(CO)_5[t\text{-}Bu\text{-}N{=}CHCH(N\text{-}t\text{-}Bu)C_4R_2R'_2]$ (5a, R = R′ = C(O)OMe)[a]

compd	C*Me*$_3$	*C*Me$_3$	N═CH	N—CH	R*C*═CR′	RC═*C*R′	alkyne R	CO's
2a[b]	28.9, 31.1	56.3, 64.4	177.3	81.3	no.	no.	127.8, 130.9	190.5, 191.6, 192.5, 196.8, 198.8, 202.7
2b[c]	29.1, 30.7	57.6, 60.4	162.0	82.8	67.3	173.8	52.2, 52.3 (OMe), 165.2, 168.4 (OC═O)	192.4, 192.5, 193.5, 194.6, 195.6, 198.1
2c[b]	29.0, 29.5	57.4, 60.1	162.7	80.1	75.5	169.1	52.0 (OMe), 167.5 (OC═O)	192.3, 193.5, 194.7, 195.3, 197.4, 198.7
2d[d]	29.0, 29.6	57.9, 60.3	163.4	82.8	63.2	181.5	125.5, 126.9, 128.7, 139.9	193.0, 194.1, 195.8, 198.3, 198.8, 199.7
3a[e]	30.1, 30.3	58.7, 64.5	172.9	75.2	no.	no.	no.	195.9, 197.6, 198.0, 201.4, 221.4 (μ-CO)
3b[e]	30.5 (2×)	58.5, 64.0	164.2	75.2	101.1	184.7	52.1, 52.8 (OMe), 173.2, 173.7 (OC═O)	196.5, 198.0, 198.4, 199.0, 203.1 (μ-CO)
3c[b]	30.7, 31.1	58.8, 63.4	164.5	74.1	109.2	179.3	52.7 (OMe), 175.4 (OC═O)	197.9, 198.6, 201.4, 203.6, 206.8 (μ-CO)
3d[c]	30.4, 31.3	58.5, 63.0	151.0	76.3	95.2	173.9	125.7, 128.8, 129.1, 139.0	198.1, 198.3, 205.3
4a[f]	30.8, 32.4	63.0, 63.5	173.9	78.2	79.9, 159.3[g]	189.8, 160.0[g]	51.9, 52.0, 52.6, 53.1 (OMe)	191.4, 193.4, 194.5, 195.2
4b[h]	30.7, 31.8	61.0, 63.3	176.6	77.2	103.7, 117.9	184.1, 141.0	128.7, 129.0, 129.6, 135.2 (Ph), 52.0, 52.3	197.3, 200.1, 201.4, 206.8
5a[c]	29.9, 30.9	57.5, 63.7	174.2	84.4	36.6, 60.7, 76.3, 138.1[g]		51.5, 51.8 (2×), 53.1	190.9, 191.9, 193.3, 196.5, 199.0

[a] Values in ppm relative to Me_4Si, measured in $CDCl_3$ solution. [b] Spectrometer frequency (SF) = 50 MHz, T = 313 K. [c] SF = 25 MHz, T = 297 K. [d] SF = 25 MHz, T = 273 K. [e] SF = 63 MHz, T = 263 K. [f] SF = 63 MHz, T = 293 K. [g] *C*C(O)OMe. [h] Measured in toluene-d_8 solution, SF = 63 MHz, T = 299 K.

were identified by IR and mass spectrometry, by elemental analyses (Table I), and by ^{1}H and ^{19}F NMR (Table II) and ^{13}C NMR (Table III). The IR and mass spectroscopy data of complexes **3b–d**, **4a,b**, and **5a** were reported previously[7] and are not included in this paper.

Synthesis of $Ru_2(CO)_6[AIB(t\text{-}Bu,CF_3,CF_3)]$ (2a). To a solution of 1 (1.5 mmol, 807 mg, prepared in situ) was condensed 3–4 equiv of hexafluorobutyne at −209 °C. The mixture was allowed to warm gradually to 4 °C. After the mixture was left standing for 48 h, yellow crystals of **2a** had precipitated, which were suitable for X-ray crystallography (yield 50–60%). When the supernatant solution was cooled to −80 °C, a second sample was obtained in 20–30% yield.

Synthesis of $Ru_2(CO)_5[AIB(t\text{-}Bu,CF_3,CF_3)]$ (3a). A solution of **2a** (1 mmol, 700 mg) in 40 mL of toluene was purged with a strong stream of nitrogen at 20 °C. After 1 h the orange-yellow color of the solution had changed to red and a virtually quantitative conversion to **3a** had occurred. The crude product was purified by column chromatography and eluted with diethyl ether as a red fraction. Crystallization from hexane/diethyl ether (1:1) at −80 °C produced a red solid in 70% yield.

Synthesis of $Ru_2(CO)_5[AIB(t\text{-}Bu,C(O)OMe,C(O)OMe)]$ (3b). A solution of 1 (1.5 mmol, 807 mg, prepared in situ) and dimethyl acetylenedicarboxylate (1.5 mmol, 213 mg) in 60 mL of heptane was stirred at 20 °C for 20 h during which the orange color of the solution gradually changes to red and an orange-red solid precipitated. The IR spectrum of the reaction mixture showed the initial formation of **2b**. During the reaction the bands of **2b** are gradually replaced by those of **3b**. The reaction mixture was evaporated to dryness and separated by column chromatography. Elution with hexane and hexane/diethyl ether (9:1) produced minor amounts of $Ru_3(CO)_{12}$ and unreacted 1, respectively. $Ru_2(CO)_5[AIB(t\text{-}Bu,C(O)OMe,C(O)OMe)]$ (**3b**) was eluted as a red fraction with diethyl ether in 60–70% yield.

Synthesis of $Ru_2(CO)_5[AIB(t\text{-}Bu,R,H)]$ (3c, R = C(O)OMe; 3d, R = Ph). A solution of 1 (1.5 mmol, 807 mg, prepared in situ) and RC≡CH (1.5 mmol; R = C(O)OMe, 126 mg; R = Ph, 153 mg) in 60 mL of heptane was stirred at 60 °C for 20 h. The reaction mixture was evaporated to dryness, and the crude product was purified by column chromatography. Elution with hexane and hexane/diethyl ether (9:1) produced minor amounts of $Ru_3(CO)_{12}$ and unreacted 1, respectively. The main product $Ru_2(CO)_5[AIB(t\text{-}Bu,R,H)]$ (3) was obtained by elution with hexane/diethyl ether (6:4 for R = Ph, 4:6 for R = C(O)OMe) in 50–60% yield.

Synthesis of $Ru_2(CO)_6[AIB(t\text{-}Bu,R,R')]$ (2b, R = R′ = C(O)OMe; 2c, R = C(O)OMe, R′ = H; 2d, R = Ph, R′ = H). A solution of **3** (1 mmol; **b**, 652 mg; **c**, 594 mg; **b**, 612 mg) in 30 mL of hexane was treated with CO (20 °C, 1 atm) for 5 min. The color of the solution changed from dark red to orange-yellow. Complexes **2** were precipitated as a microcrystalline solid at −80 °C in 90–95% yield. The NMR samples of **2** were prepared by treating a $CDCl_3$ solution with CO and were also measured under CO atmosphere.

Conversion of 2b to 3b. A solution of $Ru_2(CO)_6[AIB(t\text{-}Bu,C(O)OMe,C(O)OMe)]$ (**2b**) (1 mmol, 680 mg) in 50 mL of heptane was purged with N_2 for 1 h at 20 °C during which the color of the solution gradually changed from orange-yellow to red. The IR spectrum showed a virtually quantitative conversion to $Ru_2(CO)_5[AIB(t\text{-}Bu,C(O)OMe,C(O)OMe)]$ (**3b**), which is obtained as red crystals by crystallization at −80 °C in 80% yield.

Synthesis of $Ru_2(CO)_5[t\text{-}BuN{=}CHCH(N\text{-}t\text{-}Bu)C_2(CF_3)_2C_2(C(O)OMe)_2]$ (5b). A solution of **3a** (0.5 mmol, 336 mg) and dimethyl acetylenedicarboxylate (1 mmol, 142 mg) in 50 mL of hexane was stirred at 20 °C for 20 h. The formed orange-yellow precipitate was washed with 15 mL of diethyl ether and 20 mL of hexane and dried in vacuo. Yield: 80–85%.

Synthesis of $Ru_2(CO)_5[t\text{-}BuN{=}CHCH(N\text{-}t\text{-}Bu)C(C(O)OMe)CHCHCC(O)OMe]$ (5c). A solution of 1 (1.5 mmol, 807 mg, prepared in situ) and methyl propynoate (4.5 mmol, 378) in 60 mL of heptane was refluxed for 3 h. When in the ν_s(C═O) region of the IR spectrum of the reaction mixture the bands due to 1 had disappeared, the reaction mixture was evaporated to dryness and the crude product purified by column chromatography. Elution with hexane produced a minor amount of $Ru_3(CO)_{12}$. The major product $Ru_2(CO)_5[t\text{-}BuN{=}CHCH(N\text{-}t\text{-}Bu)C(C(O)OMe)CHCHCC(O)OMe]$ (**5c**) was obtained by elution with hexane/diethyl ether (4:6) in 50–60% yield. The same fraction contained small amounts of 1,2,4- and 1,3,5-tris(methoxycarbonyl)benzene, resulting from the cyclotrimerization of methyl propynoate. The product **5c** was recrystallized from hexane/diethyl ether (1:1) at −80 °C.

Crystal Structure Determinations of $Ru_2(CO)_6[AIB(t\text{-}Bu,CF_3,CF_3)]$ (2a) and $Ru_2(CO)_5[t\text{-}BuN{=}CHCH(N\text{-}t\text{-}Bu)C_4(C(O)OMe)_4]$ (5a). Yellow crystals of **5a** were grown by the slow evaporation in the air of a hexane/dichloromethane (1:2) solution of **5a**. The crystallographic data for **2a** and **5a** are listed in Table IV. The reflections were measured on a Nonius CAD4 diffractometer (25 °C, θ–2θ scan) using graphite monochromated Mo Kα radiation and those with an intensity below the 2.5$\sigma(I)$ level were treated as unobserved. The structures were solved by means of the heavy-atom method. The Ru atoms of **3a** were located by using the symbolic addition program set SIMPEL.[10]

Table IV. Crystallographic Data $Ru_2(CO)_6$[AIB(*t*-Bu,CF_3,CF_3)] (2a) and $Ru_2(CO)_5$[*t*-BuN=CHCHN(*t*-Bu)C_4(C(O)OMe)$_4$] (5a)

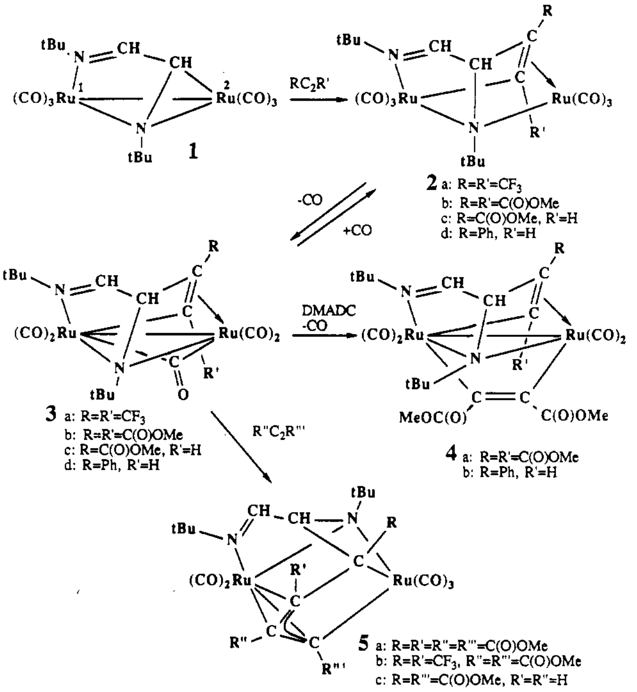
	2a	5a
formula, mol wt	$Ru_2C_{20}H_{20}N_2O_6$, 700.52	$Ru_2C_{27}H_{26}N_2O_{13}$, 794.69
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	17.475 (4)	19.694 (4)
b, Å	10.446 (2)	18.629 (3)
c, Å	13.742 (3)	18.851 (2)
α, deg	90	90
β, deg	96.05 (2)	110.378 (14)
γ, deg	90	90
V, Å^3	2494.5	6390.4
d_{calcd}, g·cm^{-1}, Z	1.87, 4	1.65, 8
μ, cm^{-1}	12.68	9.89
cryst color, size, mm^3	orange, 0.2 × 0.25 × 0.05	yellow, 0.25 × 0.15 × 0.15
radiation	Mo Kα, λ = 0.71069 Å	Mo Kα, λ = 0.71069 Å
2θ range, deg	2.2–60	2.2–40
no. of reflctns	6835	6157
no. of $I < 2.5\sigma(I)$	3476	2658
no. of reflctns in refinement	3359	3499
h min, max	−24, 24	−18, 18
k min, max	0, 14	0, 17
l min, max	0, 14	0, 17
absorptn corr	DIFABS[11]	DIFABS[11]
extinctn corr	isotropic	isotropic
weighting scheme	$w = 1/(6.14 + F_3 + 0.0237F_o^2)$	$w = 1/(3.78 + F_o + 0.039F_o^2)$
anomalous scattering	Ru	Ru
final R, R_w	0.048 (0.091)	0.052 (0.080)

The Ru atoms of **5a** were located by means of an E^2 Patterson synthesis. The C, N, O, and F atomic positions were derived from ΔF Fourier syntheses. The positions of the H atoms of **3a** were calculated and not refined, and the H atoms of **5a** were excluded. The refinement of the non-H atoms proceeded by using anisotropic block-diagonal least-squares calculations. An empirical absorption correction (DIFABS)[11] was applied. The calculations were performed with XRAY76,[12] the atomic scattering factors were taken from Cromer and Mann (1968),[13] and the dispersion correction factors were taken from ref 14.

Results and Discussion

The first type of product that is formed in the reactions of $Ru_2(CO)_6$(*t*-Bu-DAB) (**1**) with hexafluorobutyne, dimethyl acetylenedicarboxylate, methyl propynoate, or phenylacetylene is $Ru_2(CO)_6$[AIB(*t*-Bu,R,R′][8] (**2a**, R = R′ = CF_3; **2b**, R = R′ = C(O)OMe; **2c**, R = C(O)OMe, R′ = H; **2d**, R = Ph, R′ = H) (see Scheme I). This type of product results from the C–C coupling of one of the alkyne C atoms (the substituted one in the case of methyl propynoate and phenylacetylene) with the coordinated imine C atom in **1**. The second alkyne C atom has formed a Ru–C σ-bond with Ru^1 (see Scheme I). The newly formed ligand donates eight electrons to the metal carbonyl core, instead of the six electrons donated by the bridging DAB ligand in **1**. Accordingly, Ru–Ru bond, that is present in **1**, does not longer exist in **2**, which became clear from the X-ray crystal structure of **2a** which will be discussed below.

Scheme I. Reactions of $Ru_2(CO)_6$(*t*-Bu-DAB) with Alkynes



The stability of complexes **2** toward decarbonylation to give $Ru_2(CO)_5$[AIB(*t*-Bu,R,R′] (**3**) depends on the alkyne substituents. Complex **2a** is already formed at lower temperature (4 °C) and as a solid does not lose CO, even under evacuation. Heating or evacuating a solution of **2a**, however, does lead to decarbonylation to give **3a**. Compound **2b** (R = R′ = C(O)OMe) is formed from **1** at room temperature but easily loses a CO in solution and also as a solid under reduced pressure to give **3b**. The formation of **2c** and **2d** (R = C(O)OMe and Ph, respectively; R′ = H) requires elevated temperatures, under which conditions decarbonylation easily proceeds. After column chromatography of the reaction mixtures the pentacarbonyl complexes **3** are obtained as the main product. When solutions of **3** are treated with CO, the corresponding hexacarbonyl complexes **2** are formed again in high yields. Although no experimental evidence of the direct formation of **2c,d** from **1** can be obtained, we assume that their formation proceeds similar to that of **2a,b**.

The major structural differences between the complexes **2** and **3** are the presence of a metal–metal bond and a bridging CO in the latter compounds. The crystal structure of $Ru_2(CO)_5$[AIB(*t*-Bu,Ph,H)] (**3d**) (see Figure 2) was reported previously[7] and will therefore not be discussed in detail here.

The formation of $Ru_2(CO)_4$[AIB(*t*-Bu,R,R′)](μ_2-dimethyl acetylenedicarboxylate) (**4a**, R = R′ = C(O)OMe; **4b**, R = Ph, R′ = H) occurred when the corresponding complexes **3** were reacted with dimethyl acetylenedicarboxylate. This reaction, which involves the substitution of the bridging CO in **3** by a dimethyl acetylenedicarboxylate molecule, proceeds readily at 20 °C for **4a** but requires higher temperatures (>90 °C) for **4b**. The proposed molecular structure of **4a,b** as shown in Scheme I, is based on ^{1}H and ^{13}C NMR data and is different from our previous proposal.[7]

The reaction of **3b** with a second equivalent of dimethyl acetylenedicarboxylate not only results in the formation of **4a** but produces as the major product (yield >80%) $Ru_2(CO)_5$[*t*-BuN=CHCH(N-*t*-Bu)C_4(C(O)OMe)$_4$] (**5a**). The latter product results from the C–C coupling of the second alkyne with the C atom of the first alkyne that is already σ-bonded to Ru.[7] A similar product (**5b**) is formed

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(11) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(12) Stewart, J. M. The XRAY76 system, Tech. Rep. TR446; Computer Science Center, University of Maryland: College Park, MD, 1976.

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Table V. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of the Non-H Atoms of 2a (Esd's in Parentheses)

atom	x	y	z	U_{ea}, Å^2
Ru(1)	0.77580 (4)	0.21334 (7)	0.56402 (6)	0.0355 (4)
Ru(2)	0.59600 (4)	0.24874 (7)	0.45424 (6)	0.0346 (4)
C(1)	0.5344 (6)	0.369 (1)	0.3721 (8)	0.046 (6)
C(2)	0.5261 (7)	0.120 (1)	0.4113 (9)	0.057 (7)
C(3)	0.5455 (7)	0.259 (1)	0.5750 (8)	0.047 (6)
C(4)	0.8406 (7)	0.308 (1)	0.6655 (9)	0.059 (7)
C(5)	0.8287 (7)	0.057 (1)	0.6021 (9)	0.054 (7)
C(6)	0.7065 (7)	0.172 (1)	0.6555 (8)	0.056 (7)
C(7)	0.7238 (6)	0.3463 (9)	0.3906 (7)	0.036 (5)
C(8)	0.8083 (5)	0.3292 (9)	0.3834 (7)	0.036 (5)
C(9)	0.7070 (5)	0.4987 (9)	0.5269 (7)	0.036 (5)
C(10)	0.6856 (8)	0.498 (1)	0.6339 (9)	0.054 (7)
C(11)	0.7854 (7)	0.561 (1)	0.5206 (9)	0.051 (6)
C(12)	0.6439 (7)	0.583 (1)	0.4676 (10)	0.055 (7)
C(13)	0.9309 (6)	0.236 (1)	0.438 (1)	0.057 (7)
C(14)	0.9666 (9)	0.332 (2)	0.373 (1)	0.09 (1)
C(15)	0.931 (1)	0.101 (2)	0.394 (2)	0.09 (1)
C(16)	0.9770 (8)	0.239 (2)	0.541 (1)	0.08 (1)
C(17)	0.6836 (6)	0.2137 (9)	0.3669 (7)	0.036 (5)
C(18)	0.6958 (6)	0.1296 (9)	0.4526 (7)	0.040 (5)
C(19)	0.6934 (7)	−0.011 (1)	0.4447 (10)	0.056 (7)
C(20)	0.6769 (8)	0.180 (1)	0.2622 (9)	0.358 (7)
N(1)	0.8476 (5)	0.2678 (8)	0.4513 (7)	0.040 (4)
N(2)	0.7042 (4)	0.3632 (7)	0.4928 (5)	0.032 (4)
O(1)	0.4964 (6)	0.422 (1)	0.3118 (7)	0.079 (7)
O(2)	0.4830 (6)	0.043 (1)	0.3847 (8)	0.083 (7)
O(3)	0.5116 (6)	0.268 (1)	0.6411 (7)	0.075 (7)
O(4)	0.8773 (8)	0.351 (1)	0.7289 (8)	0.109 (9)
O(5)	0.8581 (6)	−0.0355 (10)	0.6254 (8)	0.082 (7)
O(6)	0.6679 (6)	0.144 (1)	0.7145 (7)	0.077 (7)
F(1)	0.6847 (5)	−0.0672 (7)	0.5310 (6)	0.077 (5)
F(2)	0.7600 (5)	−0.0619 (8)	0.4181 (7)	0.084 (6)
F(3)	0.6390 (5)	−0.0633 (7)	0.3799 (7)	0.085 (6)
F(4)	0.6198 (6)	0.0975 (9)	0.2334 (6)	0.090 (6)
F(5)	0.7386 (7)	0.124 (1)	0.2340 (7)	0.122 (9)
F(6)	0.6625 (7)	0.2780 (8)	0.2040 (5)	0.091 (6)

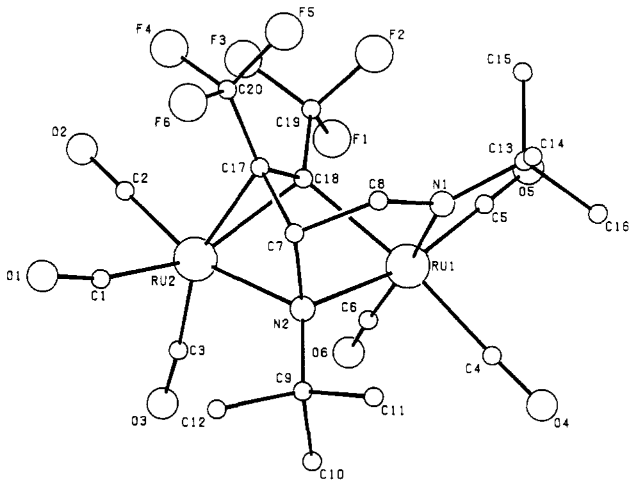


Figure 1. PLUTO drawing of $Ru_2(CO)_6$[AIB(*t*-Bu,CF_3,CF_3) (**2a**). The H atoms are omitted for clarity.

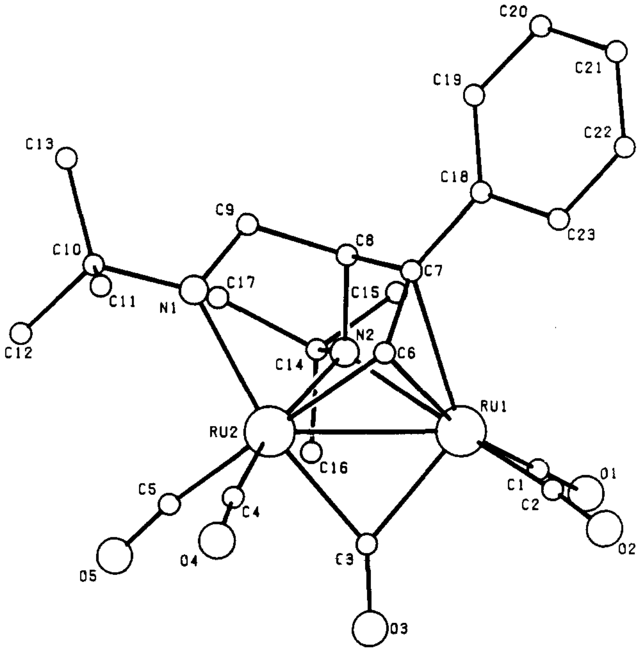


Figure 2. PLUTO drawing of $Ru_2(CO)_5$[AIB(*t*-Bu,Ph,H)] (**3d**).

when **3a** is reacted with dimethyl acetylenedicarboxylate at 20 °C. Complex **5c** is formed when 1 is reacted with more than 1 equiv of methyl propynoate at 96 °C but also when **2c** or **3c** is reacted with 1 equiv of methyl propynoate. The X-ray structure of **5a** showed that in the complexes **5** the C atoms of the second alkyne and the alkyne C atom to which it is coupled form an η^3-allyl function and that there is no Ru–Ru bond. This crystal structure will also be discussed below.

Molecular Structure of $Ru_2(CO)_6$[AIB(*t*-Bu,CF_3,CF_3)] (2a). The molecular structure of **2a** consists of two $Ru(CO)_3$ units which are linked by a formally 8e donating bridging organic ligand resulting from the C–C coupling of the DAB ligand and a hexafluorobutyne molecule. The length of the newly formed C(7)–C(17) bond of 1.572 (10) Å is normal for a single C–C bond. The AIB ligand is bonded to Ru(1) via a σ-N donor bond [Ru(1)–N(1) = 2.170 (7) Å], a σ-Ru–N covalent bond [Ru(1)–N(2) = 2.172 (6) Å], and a Ru–C σ-bond [Ru(1)–C(18) = 2.148 (8) Å]. Ru(2) is bonded via the η^2-C=C coordinated reduced alkyne bond [Ru(2)–C(17) = 2.075 (7) Å; Ru(2)–C(18) = 2.145 (8) Å, C(17)–C(18) = 1.467 (10) Å] and via the σ-bonded N donor atom N(2) [Ru(2)–N(2) = 2.253 (6) Å]. The CO ligands are all terminally bonded with usual bond lengths and angles. The Ru(1)···Ru(2) distance of 3.359 (4) Å clearly indicates the absence of a bonding Ru–Ru interaction.

Molecular Structure of $Ru_2(CO)_5$[*t*-BuN=CHCH(N-*t*-Bu)C_4(C(O)OMe)$_4$] (5a). In the crystal structure of **5a** the asymmetric unit contains two independent molecules, which differ with respect to the orientation of the C(O)OMe substituent on C(18), but have basically the same molecular geometry. In the following discussion we will therefore only discuss the features of molecule 2. The molecular structure of **5a** consists of a $Ru(CO)_2$ and a $Ru(CO)_3$ unit, with terminally bonded CO ligands, which are bridged by a formally 10e donating organic ligand resulting from the C–C coupling of the DAB ligand and two dimethyl acetylenedicarboxylate molecules. Also this compound shows a nonbonding Ru···Ru distance of

Table VI. Selected Bond Lengths (Å) of the Non-H Atoms of 2a (Esd's in Parentheses)

Ru(1)···Ru(2)	3.359 (4)	Ru(2)–N(2)	2.253 (6)	C(13)–N(1)	1.52 (1)
Ru(1)–C(18)	2.148 (8)	C(7)–C(8)	1.50 (1)	C(17)–C(18)	1.467 (10)
Ru(1)–N(1)	2.170 (7)	C(7)–C(17)	1.572 (10)	C(17)–C(20)	1.47 (1)
Ru(1)–N(2)	2.172 (6)	C(7)–N(2)	1.491 (9)	C(18)–C(19)	1.47 (1)
Ru(2)–C(17)	2.075 (7)	C(8)–N(1)	1.272 (9)	C–F(av)	1.34 (1)
Ru(2)–C(18)	2.145 (8)	C(9)–N(2)	1.490 (8)		

Table VII. Selected Bond Angles (deg) of the Non-H Atoms of 2a (Esd's in Parentheses)

C(18)–Ru(1)–N(1)	88.4 (4)	Ru(1)–C(18)–Ru(2)	103.0 (4)
C(18)–Ru(1)–N(2)	70.8 (4)	Ru(1)–C(18)–C(17)	110.9 (6)
N(1)–Ru(1)–N(2)	80.7 (3)	Ru(1)–C(18)–C(19)	118.0 (6)
C(17)–Ru(2)–C(18)	40.6 (4)	Ru(2)–C(18)–C(17)	67.1 (6)
C(17)–Ru(2)–N(2)	65.0 (4)	Ru(2)–C(18)–C(19)	124.2 (6)
C(18)–Ru(2)–N(2)	69.3 (4)	C(17)–C(18)–C(19)	122.5 (8)
C(8)–C(7)–C(17)	107.6 (8)	Ru(1)–N(1)–C(8)	110.3 (6)
C(8)–C(7)–N(2)	113.7 (7)	Ru(1)–N(1)–C(13)	131.3 (5)
C(17)–C(7)–N(2)	99.1 (7)	C(8)–N(1)–C(13)	118.1 (8)
C(7)–C(8)–N(1)	118.1 (8)	Ru(1)–N(2)–Ru(2)	98.8 (3)
Ru(2)–C(17)–C(7)	93.8 (6)	Ru(1)–N(2)–C(7)	99.2 (5)
Ru(2)–C(17)–C(18)	72.2 (6)	Ru(1)–N(2)–C(9)	123.0 (5)
Ru(2)–C(17)–C(20)	128.3 (6)	Ru(2)–N(2)–C(7)	89.2 (5)
C(7)–C(17)–C(18)	109.7 (7)	Ru(2)–N(2)–C(9)	125.2 (5)
C(7)–C(17)–C(20)	113.6 (7)	C(7)–N(2)–C(9)	113.9 (6)
C(18)–C(17)–C(20)	129.1 (7)		

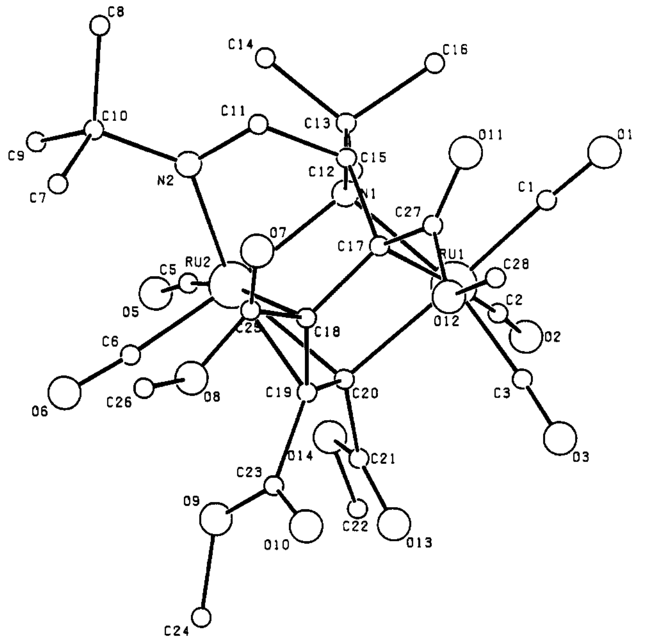


Figure 3. PLUTO drawing of molecule 2 of $Ru_2(CO)_5[t\text{-}BuN{=}CHCH(N\text{-}t\text{-}Bu)C_4(C(O)OMe)_4]$ (**5a**).

3.3095(19)Å. The N atom of the intact imino group is σ-bonded as a 2e donor [Ru(2)–N(2) = 2.147 (9) Å]. The second N atom is symmetrically bridging both metal centers [Ru(1)–N(1) = 2.137 (9) Å; Ru(2)–N(1) = 2.182 (9) Å]. The alkyne C(17) atom of the first dimethyl acetylenedicarboxylate that is coupled to the DAB is σ-bonded to Ru(1)[Ru(1)–C(17) = 2.179 (11) Å]. The second dimethyl acetylenedicarboxylate is C–C coupled to the other alkyne C atom (C(18)) of the first dimethyl aceylenedicarboxylate and forms an allyl fragment that is η^3-coordinated to Ru(2) [Ru(2)–C(18) = 2.297 (12) Å; Ru(2)–C(19) = 2.279 (12) Å; Ru(2)–C(20) = 2.185 (11) Å] and is σ-bonded to Ru(1)

Table VIII. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of the Non-H Atoms of 5a (Esd's in Parentheses)

atom	x	y	z	U_{eq}, Å^2	atom	x	y	z	U_{eq}, Å^2
Ru(1)	0.42228 (7)	0.34713 (7)	0.44502 (8)	0.0333 (9)	Ru(1*)	0.29961 (7)	0.12871 (7)	0.01057 (8)	0.0332 (8)
Ru(2)	0.30655 (7)	0.23393 (7)	0.47646 (7)	0.0244 (8)	Ru(2*)	0.42104 (7)	0.23475 (7)	−0.02120 (7)	0.0279 (8)
C(1)	0.4417 (10)	0.3855 (9)	0.3588 (9)	0.05 (1)	C(1*)	0.2769 (10)	0.1009 (9)	0.0999 (9)	0.04 (1)
C(2)	0.412 (1)	0.4400 (9)	0.4843 (10)	0.05 (1)	C(2*)	0.3059 (10)	0.0328 (10)	−0.0254 (9)	0.05 (1)
C(3)	0.5232 (10)	0.3472 (9)	0.5061 (10)	0.04 (1)	C(3*)	0.2013 (9)	0.132 (1)	−0.047 (1)	0.05 (1)
C(5)	0.2352 (9)	0.2851 (9)	0.5049 (10)	0.03 (1)	C(5*)	0.4904 (9)	0.1797 (10)	−0.0449 (9)	0.04 (1)
C(6)	0.2960 (9)	0.1646 (8)	0.5411 (8)	0.035 (10)	C(6*)	0.4343 (9)	0.305 (1)	−0.0881 (9)	0.04 (1)
C(7)	0.2344 (9)	0.047 (1)	0.384 (1)	0.06 (1)	C(7*)	0.4969 (9)	0.423 (1)	0.064 (1)	0.06 (1)
C(8)	0.151 (1)	0.113 (1)	0.261 (1)	0.07 (1)	C(8*)	0.567 (1)	0.363 (1)	0.194 (1)	0.09 (2)
C(9)	0.1389 (9)	0.1398 (9)	0.390 (1)	0.05 (1)	C(9*)	0.5907 (9)	0.328 (1)	0.073 (1)	0.06 (1)
C(10)	0.1957 (9)	0.118 (1)	0.3507 (10)	0.05 (1)	C(10*)	0.5333 (8)	0.3539 (9)	0.1022 (9)	0.03 (1)
C(11)	0.2817 (8)	0.1973 (8)	0.3226 (9)	0.03 (1)	C(11*)	0.4433 (8)	0.2797 (9)	0.1322 (8)	0.030 (10)
C(12)	0.3350 (8)	0.2551 (8)	0.3410 (9)	0.031 (9)	C(12*)	0.3883 (7)	0.2208 (7)	0.1101 (8)	0.017 (8)
C(13)	0.2537 (10)	0.3589 (10)	0.345 (1)	0.05 (1)	C(13*)	0.471 (1)	0.1137 (9)	0.1137 (10)	0.05 (1)
C(14)	0.1812 (10)	0.320 (1)	0.299 (1)	0.07 (1)	C(14*)	0.5412 (10)	0.152 (1)	0.158 (1)	0.06 (1)
C(15)	0.235 (1)	0.413 (1)	0.402 (1)	0.08 (2)	C(15*)	0.479 (1)	0.053 (1)	0.061 (1)	0.06 (1)
C(16)	0.275 (1)	0.4063 (10)	0.284 (1)	0.06 (1)	C(16*)	0.4457 (10)	0.0740 (9)	0.1764 (10)	0.05 (1)
C(17)	0.4094 (8)	0.2376 (8)	0.3979 (9)	0.026 (9)	C(17*)	0.3125 (8)	0.2395 (8)	0.0506 (8)	0.027 (9)
C(18)	0.4102 (8)	0.1897 (8)	0.4646 (8)	0.027 (9)	C(18*)	0.3159 (8)	0.2848 (8)	−0.0169 (8)	0.029 (10)
C(19)	0.4232 (7)	0.2211 (8)	0.5385 (8)	0.025 (9)	C(19*)	0.3010 (9)	0.2507 (8)	−0.0891 (9)	0.027 (10)
C(20)	0.4089 (9)	0.2902 (9)	0.5406 (9)	0.03 (1)	C(20*)	0.3203 (8)	0.1784 (8)	−0.0833 (9)	0.028 (9)
C(21)	0.426 (1)	0.3337 (9)	0.6135 (10)	0.05 (1)	C(21*)	0.2998 (8)	0.1329 (10)	−0.12585 (9)	0.04 (1)
C(22)	0.393 (1)	0.431 (1)	0.678 (1)	0.09 (2)	C(22*)	0.334 (1)	0.041 (1)	−0.222 (1)	0.07 (2)
C(23)	0.4613 (8)	0.1836 (9)	0.6163 (9)	0.04 (1)	C(23*)	0.2680 (9)	0.2876 (10)	−0.1650 (9)	0.04 (1)
C(24)	0.465 (1)	0.167 (1)	0.743 (1)	0.08 (2)	C(24*)	0.267 (1)	0.293 (1)	−0.294 (1)	0.08 (2)
C(25)	0.4126 (7)	0.1106 (8)	0.4583 (8)	0.027 (9)	C(25*)	0.3183 (8)	0.3632 (8)	−0.0063 (9)	0.030 (10)
C(26)	0.423 (1)	0.013 (1)	0.381 (1)	0.07 (2)	C(26*)	0.305 (1)	0.4751 (9)	−0.072 (1)	0.08 (1)
C(27)	0.4621 (8)	0.2191 (8)	0.3607 (9)	0.031 (10)	C(27*)	0.2619 (8)	0.2649 (9)	0.0873 (9)	0.03 (1)
C(28)	0.582 (1)	0.174 (1)	0.373 (1)	0.08 (2)	C(28*)	0.1512 (10)	0.327 (1)	0.078 (1)	0.08 (2)
N(1)	0.3137 (6)	0.3097 (6)	0.3912 (7)	0.030 (8)	N(1*)	0.4091 (6)	0.1627 (7)	0.0662 (8)	0.034 (8)
N(2)	0.2524 (6)	0.1783 (6)	0.3705 (7)	0.026 (7)	N(2*)	0.4728 (7)	0.2940 (7)	0.0826 (7)	0.034 (8)
O(1)	0.4584 (8)	0.4097 (8)	0.3107 (8)	0.07 (1)	O(1*)	0.2594 (9)	0.0862 (7)	0.1509 (8)	0.09 (1)
O(2)	0.4098 (9)	0.4977 (8)	0.5071 (10)	0.10 (1)	O(2*)	0.3064 (9)	−0.0234 (7)	−0.0519 (8)	0.08 (1)
O(3)	0.5832 (7)	0.3432 (8)	0.5406 (8)	0.08 (1)	O(3*)	0.1415 (7)	0.1346 (7)	−0.0883 (7)	0.066 (9)
O(5)	0.1955 (6)	0.3083 (7)	0.5309 (6)	0.057 (8)	O(5*)	0.5303 (7)	0.1517 (7)	−0.0693 (8)	0.068 (10)
O(6)	0.2828 (6)	0.1218 (6)	0.5818 (6)	0.050 (8)	O(6*)	0.4488 (7)	0.3441 (8)	−0.1290 (7)	0.066 (9)
O(7)	0.4148 (7)	0.0701 (6)	0.5092 (7)	0.058 (8)	O(7*)	0.3216 (7)	0.3916 (7)	0.0527 (7)	0.052 (8)
O(8)	0.4102 (6)	0.0897 (6)	0.3885 (6)	0.043 (7)	O(8*)	0.3179 (6)	0.3983 (6)	−0.0688 (6)	0.043 (7)
O(9)	0.4254 (6)	0.1868 (7)	0.6626 (6)	0.047 (8)	O(9*)	0.3078 (6)	0.2777 (7)	−0.2099 (6)	0.054 (8)
O(10)	0.5195 (6)	0.1557 (7)	0.6310 (7)	0.057 (8)	O(10*)	0.2080 (6)	0.3111 (8)	−0.1844 (7)	0.065 (9)
O(11)	0.4550 (6)	0.204 (7)	0.2958 (6)	0.048 (8)	O(11*)	0.2721 (6)	0.2570 (6)	0.1560 (6)	0.045 (7)
O(12)	0.5272 (6)	0.1946 (7)	0.4101 (6)	0.050 (8)	O(12*)	0.2017 (6)	0.2927 (7)	0.0406 (6)	0.040 (7)
O(13)	0.4808 (7)	0.3317 (8)	0.6628 (7)	0.074 (10)	O(13*)	0.2435 (16)	0.1311 (8)	−0.2049 (7)	0.061 (9)
O(14)	0.3741 (7)	0.3795 (6)	0.6152 (7)	0.053 (8)	O(14*)	0.3579 (6)	0.0916 (7)	−0.1576 (6)	0.054 (8)

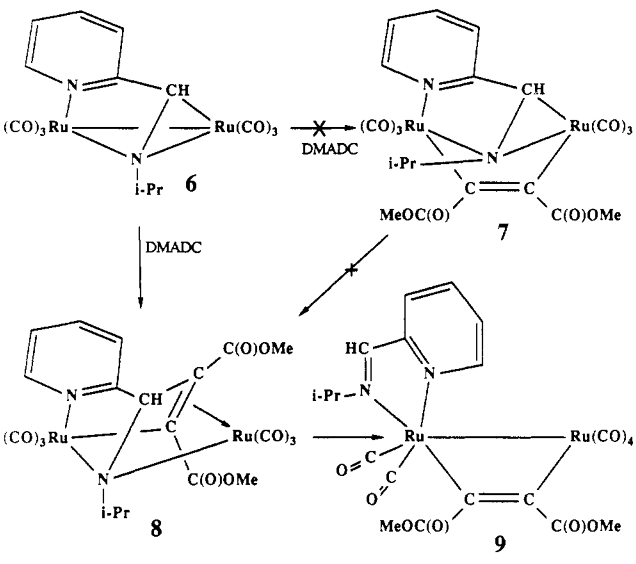
Table IX. Selected Bond Lengths (Å) of the Non-H Atoms of Molecule 2 of 5a (Esd's in Parentheses)

Ru(1)···Ru(2)	3.3095 (19)	Ru(2)–N(1)	2.182 (9)	C(17)–C(18)	1.532 (15)
Ru(1)–C(12)	2.677 (10)	Ru(2)–N(2)	2.147 (9)	C(17)–C(27)	1.468 (16)
Ru(1)–C(17)	2.179 (11)	C(10)–N(2)	1.580 (15)	C(18)–C(19)	1.420 (15)
Ru(1)–C(20)	2.135 (11)	C(11)–C(12)	1.495 (15)	C(18)–C(25)	1.472 (15)
Ru(1)–N(1)	2.137 (9)	C(11)–N(2)	1.227 (15)	C(19)–C(20)	1.393 (15)
Ru(2)–C(18)	2.297 (12)	C(12)–C(17)	1.557 (15)	C(19)–C(23)	1.499 (16)
Ru(2)–C(19)	2.279 (12)	C(12)–N(1)	1.496 (13)	C(20)–C(21)	1.562 (16)
Ru(2)–C(20)	2.185 (11)	C(13)–N(1)	1.533 (16)		

Table X. Selected Bond Angles (deg) of the Non-H Atoms of Molecule 2 of 5a (Esd's in Parentheses)

C(17)–Ru(1)–C(20)	80.5 (6)	Ru(2)–C(18)–C(25)	114.8 (9)
C(17)–Ru(1)–N(1)	64.9 (5)	C(17)–C(18)–C(19	118.3 (12)
C(20)–Ru(1)–N(1)	79.6 (6)	C(17)–C(18)–C(25)	116.4 (11)
C(18)–Ru(2)–C(19)	36.1 (5)	C(19)–C(18)–C(25)	123.8 (11)
C(18)–Ru(2)–C(20)	63.2 (6)	Ru(2)–C(19)–C(18)	72.7 (10)
C(18)–Ru(2)–N(1)	83.8 (5)	Ru(2)–C(19)–C(20)	68.2 (10)
C(18)–Ru(2)–N(2)	84.9 (5)	Ru(2)–C(19)–C(23)	127.4 (9)
C(19)–Ru(2)–C(20)	36.2 (5)	C(18)–C(19)–C(20)	113.5 (12)
C(19)–Ru(2)–N(1)	97.6 (6)	C(18)–C(19)–C(23)	124.3 (12)
C(19)–Ru(2)–N(2)	120.5 (5)	C(20)–C(19)–C(23)	122.2 (11)
C(20)–Ru(2)–N(1)	77.5 (6)	Ru(1)–C(20)–Ru(2)	100.0 (6)
C(20)–Ru(2)–N(2)	141.4 (4)	Ru(1)–C(20)–C(19)	111.0 (10)
N(1)–Ru(2)–N(2)	77.8 (5)	Ru(1)–C(20)–C(21)	115.6 (9)
C(12)–C(11)–N(2)	115.0 (12)	Ru(2)–C(20)–C(19)	75.5 (10)
C(11)–C(12)–C(17)	117.0 (11)	Ru(2)–C(20)–C(21)	129.6 (8)
C(11)–C(12)–N(1)	111.8 (11)	C(19)–C(20)–C(21)	118.5 (12)
C(17)–C(12)–N(1)	98.7 (11)	Ru(1)–N(1)–Ru(2)	100.0 (5)
Ru(1)–C(17)–C(12)	90.0 (9)	Ru(1)–N(1)–C(12)	93.2 (8)
Ru(1)–C(17)–C(18)	106.0 (9)	Ru(1)–N(1)–C(13)	124.6 (9)
Ru(1)–C(17)–C(27)	116.5 (9)	Ru(2)–N(1)–C(12)	94.7 (8)
C(12)–C(17)–C(18)	113.6 (11)	Ru(2)–N(1)–C(13)	121.7 (8)
C(12)–C(17)–C(27)	112.4 (12)	C(12)–N(1)–C(13)	115.5 (11)
C(18)–C(17)–C(27)	115.6 (11)	Ru(2)–N(2)–C(10)	130.9 (7)
Ru(2)–C(18)–C(17)	95.8 (10)	Ru(2)–N(2)–C(11)	110.4 (9)
Ru(2)–C(18)–C(19)	71.2 (10)	C(10)–N(2)–C(11)	118.5 (11)

Scheme II. Reactions of $Ru_2(CO)_6$(*i*-Pr-Pyca) with Dimethyl Acetylenedicarboxylate



[Ru(1)–C(20) = 2.135(11)Å].

The structure of **5a** may be regarded as the result of the insertion of the second dimethyl acetylenedicarboxylate molecule between the olefinic fragment and the Ru center to which it is η^2-C=C bonded in **3b**. The geometry of the bridging ligand is reminiscent of the organic ligands that are formed by the coupling of three alkynes in dinuclear complexes.[15] The presence of an imine fragment instead of a third alkyne coupled to the $C_4(C(O)OMe)_4$ fragment results in the coordination of the N(1)–C(12)–C(17) part of the ligand to Ru(1) via a dative N(1)–Ru(1) bond and a Ru(1)–C(17) σ-bond, instead of coordination via a second allyl function, as is observed in the case of three coupled alkynes. The bis(allyl) ligands and the ligand in **5a** can be considered to be isoelectronic since, when regarded as neutral ligands, they both donate eight electrons to the metal centers.

NMR Spectroscopy. When we compare the ^1H NMR chemical shifts of the complexes **2a–d** with those of **3a–d**, the most striking differences are the upfield shifts of about 1 ppm for the imine protons and about 0.4 ppm for the amine protons. Complex **2a** is an exception since the imine chemical shift is almost identical with that in **3a**. The generally observed upfield shifts are in agreement with the earlier mentioned increased back-bonding to the AIB ligand in **2**. The different behavior of **2a** is possibly related to the strong electron-withdrawing effect of the CF_3 groups, which strongly influences the chemical shift of the N–C(H) fragments. The ^1H chemical shifts of **5b** and **5c** are comparable with those earlier reported for **5a**.[7] A small upfield shift is observed for **5b** relative to **5a** due to the two C(O)OMe groups which are replaced by two more electron-withdrawing CF_3 groups.

Complex Formation. All presently discussed reactions of **1** with alkynes have as a common initial reaction step, the formation of $Ru_2(CO)_6$[AIB(*t*-Bu,R,R′)] (**2**). We propose that its formation proceeds via a direct electrophilic attack of the alkyne on the coordinated imine C atom and the Ru center to which both N atoms of the DAB ligand are bonded in **1**. Concomitantly the Ru–Ru bond is ruptured and the alkyne bond, which is reduced to an olefinic fragment, is η^2-C=C coordinated to the second Ru center. A second possibility is the initial insertion of the alkyne in the Ru–Ru bond in **1** followed by the C–C coupling with the DAB ligand. This, however, appears to be less likely, since the reaction of $Ru_2(CO)_6$(*i*-Pr-Pyca),[16] which is isostructural with **1**, with dimethyl acetylenedicarboxylate gives the product $Ru_2(CO)_6$(*i*-Pr-Pyca)(μ_2-dimethyl acetylenedicarboxylate) (**9**) via the initial formation of an intermediate complex **8** which is isostructural to **2** (see Scheme II). There is no reason to assume that **8** is formed via an intermediate **7**, with a μ_2-bridging dimethyl acetylenedicarboxylate which would subsequently be coupled to the Pyca ligand, after which the formed C–C bond would be broken again to give **9** with a chelating Pyca ligand and a μ_2-bridging dimethyl acetylenedicarboxylate.[17]

The electrophilic character of the attack of the alkyne is in agreement with several observations. The reaction

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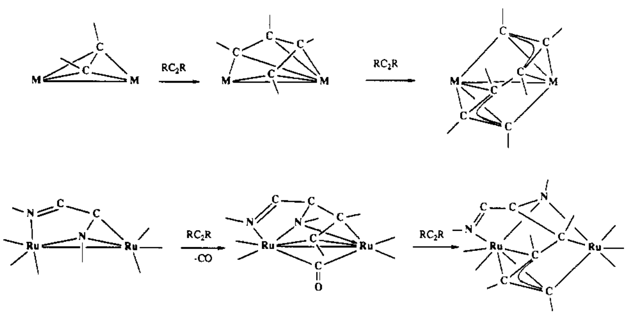
(15) (a) Knox, S. A. R.; Stansfield, R. D. F.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 173. (b) Pourreau, D. B.; Whittle, R. R.; Geoffroy, G. L. *J. Organomet. Chem.* **1984**, *273*, 333. (c) Dickson, R. S.; Fraser, P. J.; Gatehouse, B. M. *J. Chem. Soc., Dalton Trans.* **1972**, 2278. (d) Mays, M.; Prest, D. W.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1981**, 771. (e) Brammer, L.; Green, M.; Orpen, A. G.; Paddick, K. E.; Saunders, D. R. *J. Chem. Soc., Dalton Trans.* **1986**, 657.

(16) R-Pyca is the abbreviation for pyridinecarbaldimine, which is C_5H_4N-2-CH=NR.

(17) The $Ru_2(CO)_6$(R-Pyca)/alkyne chemistry will be discussed in part 10 of this series: Muller, F.; van Koten, G.; Vrieze, K.; Heijdenrijk, D.; Kragten, E.; Stam, C. H., Zoutberg, M. C. *Organometallics*, in press.

(18) Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*(1), 126.

Scheme III. Comparison between the Coupling of Alkynes and the Coupling of R-DAB with Alkynes



of $Ru_2(CO)_6$(*i*-Pr-DAB) with $MeC{\equiv}CNEt_2$, of which the alkyne C atom have a δ^- polarizations due to the mesomeric electron-donating amino substituent and are hence less electrophilic, does not lead to a C–C coupling as in **2**. Instead the substitution of the η^2-C=N bonded imine by an alkyne occurs.[2] Further, the reaction rates of the reactions of **1** with alkynes decrease with decreasing substitution with electron withdrawing substituents in the order of hexafluorobutyne > dimethyl acetylenedicarboxylate > methyl propynoate > phenylacetylene. Finally, the C–C coupling of the alkyne with the coordinated imine C atom only takes place in the case of η^2-C=N coordination to Ru and not when the imine is coordinated to Fe. Such behavior is expected since Fe exhibits less back-bonding to a η^2-bonded organic ligand than Ru, and hence the nucleophilicity of the coordinated imine fragment is reduced appreciably in the case of Fe.

The substitution of the bridging CO ligand in **3** by a dimethyl acetylenedicarboxylate molecule to give **4a,b** (see Scheme I) is not an unprecedented reaction. A similar process is observed when $M_2(CO)_5$(R-DAB(8e)), which also contains a bridging organic ligand (i.e. an 8e donating R-DAB ligand) and a bridging CO, is reacted with an alkyne. The bridging CO is then substituted by a μ_2-bridging alkyne to give $M_2(CO)_4$(R-DAB(8e))(μ_2-alkyne).[6b,c]

As in the formation of **2**, the reaction of **3** with a second alkyne molecule to give **5** most likely proceeds via a direct electrophilic attack of the second alkyne on the first alkyne fragment and the Ru center with the η^2-C=C olefinic ligand. This is in agreement with the observation that this type of reaction only occurs in the case of alkynes bearing electron-withdrawing substituents. Complex **3d**, derived from phenylacetylene, reacts with dimethyl acetylenedicarboxylate to give only **4b** and no products of type **5**.

The reaction sequence **1** → **3** → **5** shows a remarkable resemblance with the "classical" transition metal/alkyne chemistry. In the past a number of reactions of dinuclear transition-metal complexes with alkynes have been reported, in which the bridging alkyne reacts with a second alkyne to give a butadienediyl fragment, which then reacts with a third alkyne to give a C_6R_6 bis(allyl) ligand.[15]

In this respect we can compare the 4e donating η^2-C=N bonded imine fragment in **1** with a μ_2,η^2-C≡C bonded 4e donating alkyne molecule bridging two metal centers (see Scheme III). The direct electrophilic attack of the first alkyne on the coordinated imine C atom resulting in a C–C bond formation to give **2** followed by the loss of a CO to give **3** is then comparable with the formation of metallacyclopentadienyl complexes via a direct attack of the alkyne on the μ_2,η^2-bonded alkyne in a dinuclear complex, as was proposed by Hoffmann et al.[18] This is corroborated by the crystal structure of **3d** (see Figure 3) which is reminiscent of several structurally characterized metallacyclopentadienyl complexes.[19]

The resemblance of complexes **5** with the above-mentioned $M_2L_x(C_6R_6)$ bis(allyl) complexes was already pointed out in the discussion of the crystal structure of **5a** (vide supra). Also in this case there is a C–C coupled imine fragment instead of the third alkyne, although the N(1)–C(17)–C(12) part of the ligand donates the same number of electrons to the Ru(1) center as would be the case with an η^3-allyl ligand.

Another remarkable aspect of the reaction sequence **1** → **2** → **3** → **5** is the initial fission of the Ru–Ru bond (**1** → **2**), which in the next step is restored (**2** → **3**) to be subsequently broken again (**3** → **5**). Such a flexible accommodation of the metal–metal interaction to the number of electrons donated to the metal carbonyl core by the ligands was also observed in the above-mentioned sequential linking of alkynes at dichromium and dimolybdenum centers.[15] This flexibility of the metal–metal interactions in the presently reported Ru complexes not only plays a crucial role in the ability of these complexes to give the observed C–C coupling processes but also indicates the general importance of the adaption of the metal–metal interactions in (catalytic) conversions of organic substrates on polynuclear metal fragments.

Finally, it is of importance to note that, due to the presence of bridging ligands, the dinuclear character of the reported compounds is maintained during all conversions, irrespective of the presence or absence of a direct metal–metal bond.

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Registry No. 1, 74552-68-4; **2a**, 119454-74-9; **2b**, 119454-75-0; **2c**, 119454-76-1; **2d**, 119454-77-2; **3a**, 119454-78-3; **3b**, 78199-22-1; **3c**, 78199-24-3; **3d**, 78199-19-6; **4a**, 78199-35-6; **4b**, 78217-08-0; **5a**, 119454-79-4; **5b**, 119454-80-7; **5c**, 119454-81-8; **6**, 107148-68-5; **9**, 119435-48-2; $F_3CC{\equiv}CCF_3$, 692-50-2; MeOCOC≡CCOOMe, 762-42-5; HC≡CCOOMe, 922-67-8; HC≡CPh, 536-74-3.

Supplementary Material Available: A table of the anisotropic thermal parameters of the non-H atoms, a table of the calculated fractional coordinates of the H atoms, a full listing of bond lengths and angles of the non-H atoms, and a stereoscopic ORTEP representation for **2a** and a table of the anisotropic thermal parameters of the non-H atoms, a full listing of the bond lengths and angles of the non-H atoms, and a stereoscopic ORTEP representation for **5a** (9 pages); listings of observed and calculated structure factors for **2a** and **5a** (41 pages). Ordering information is given on any current masthead page.

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(19) Part 4 of this series: Muller, F.; Han, I. M.; van Koten, G.; Vrieze, K.; Heijdenrijk, D.; de Jong, R. L.; Zoutberg, M. C. *Inorg. Chim. Acta*, in press.