1158 *Organometallics* **1984**, *3*, 1158-1163

Coupling of 1-(Diethylamino)propyne on Dodecacarbonyltriiron and Dodecacarbonyltriruthenium: Formation of $[Fe_2(CO)_6\{C_4(CH_3)_2[N(C_2H_5)_2]_2\}]$ Containing a Metallacyclopentadiene Fragment with Tail-to-Tail Coupling and Formation of $[Ru_4(CO)_8\{C_5O(CH_3)_2[N(C_2H_5)_2]_2\}_2]$ Containing a Cyclopentadienone with Head-to-Tail Coupling

Jean-Claude Daran* and Yves Jeannin

Laboratoire de Chimie des Métaux de Transition, E.R.A. 608, Université Pierre et Marie Curie, 75230 Paris Cedex 05, France

Received December 27, 1983

Syntheses and single-crystal X-ray diffraction studies have been completed on three derivatives isolated from the reaction of 1-(diethylamino)propyne with dodecacarbonyltriiron and dodecacarbonyltriruthenium. Crystal data for compound I, $[Fe_2(CO)_6\{C_4(CH_3)_2[N(C_2H_5)_2]_2\}]$: monoclinic, space group $P2_1/c$, a = 16.001 (5) Å, b = 11.209 (1) Å, c = 13.550 (9) Å, β = 103.64 (7)°, R_w = 0.0655 for 2658 reflections. Crystal data for compound II, $[Ru_4(CO)_8\{C_5O(CH_3)_2[N(C_2H_5)_2]_2\}_2]$: monoclinic, space group $P2_1/n$, a = 14.135 (1) Å, b = 14.158 (1) Å, c = 10.696 (1) Å, β = 97.55 (1)°, R_w = 0.041 for 2924 reflections. Crystal data for compound III, same formula as II: monoclinic, space group $P2_1/n$, a = 8.059 (3) Å, b = 16.440 (9) Å, c =16.05 (1) Å, β = 96.65 (6)°, R_w = 0.0361 for 2510 reflections. Compound I is another example of metallacyclopentadiene complexes; it results from a tail-to-tail coupling of the aminoalkyne; the overall geometry is strongly modified by nitrogen atoms when compared with other metallacyclopentadienes. Compounds II and III are tetranuclear species; they are identical, but two ethyl groups attached to one nitrogen are disordered in II. The whole molecule has an inversion center that relates two dimetallic subunits containing a metal-metal bond, through a double oxygen bridge; these oxygens belong to two groups resembling a cyclopentadienolato ligand, which results from a head-to-tail coupling of the aminoalkyne. One amino group among the two is ligated.

Introduction

Reactions of alkynes with metal carbonyls have been widely investigated and have led to numerous organometallic derivatives. In this large field, our interest in modelling the inhibition of corrosion of a metal surface by organic substances led us to consider the reaction of acetylenic alcohols known as good corrosion inhibitors toward carbonyl clusters that may be regarded as models for a surface.[1] The results demonstrate that alcohol groups do not play a particular role in the formation of the complexes that are well-known metallacycle compounds.[2] We then became interested in the possible modification of reactivity by utilization of functionalized alkynes such as aminoalkyne $R'C{\equiv}CNR_2$. Protonation of these ligands, which occurs on the carbon atom CR′,[3] suggests the mesomeric structures

$$R'C{\equiv}CNR_2 \qquad R'C^-{=}C{=}^+NR_2$$

Thus, the increased negative charge on the CR′ carbon atom makes the reactivity of aminoalkynes toward metal carbonyls different from that of simple alkynes, as was shown by King and Harmon.[4] However, X-ray structural determinations on organometallic complexes obtained after reaction of aminoalkynes are scanty and concern, to the best of our knowledge, one (cyclobutadiene)palladium complex[5] and one (aminocarbene)chromium complex.[6]

It may be noted that a similar formal charge separation could be assigned to the corresponding group 5 derivatives $R'C{\equiv}CPR_2$ that have recently received a great deal of attention;[7] however, the phosphinoalkyne chemistry is dominated by the fracture of the C-P bond; this does not seem to be the case in the aminoalkyne chemistry. Due to its d orbital, phosphorus tends to react as an acceptor while nitrogen tends to behave as a donor.

This paper deals with syntheses and X-ray structural studies of three complexes obtained from the reactions of 1-(diethylamino)propyne with dodecacarbonyltriiron and dodecarbonyltriruthenium.

Experimental Section

Syntheses. Reaction of $CH_3C{\equiv}CN(C_2H_5)_2$ with $Fe_3(CO)_{12}$. 1-(Diethylamino)propyne (111 mg, 1.4 mmol) was added to a solution of $Fe_3(CO)_{12}$ (710 mg, 1.4 mmol) in 100 mL of tetrahydrofuran. The solution was stirred at room temperature (20 °C) for 4 h under dry nitrogen. Chromatography of the solution on a 80 × 2 cm deactivated silica gel column with petroleum ether/THF mixture eluted a yellow band. Evaporation, followed by recrystallization from THF, afforded orange crystals of I (150 mg, 21%): IR ν(CO) 2060 (s), 2010 (s), 1975 (s), 1970 (s), 1958 (s), 1885 (s) cm^{-1}; ^{1}H NMR($CDCl_3$) δ 1.12 (t, 3 H), 2.25 (s, 3 H), 3.22 (q, 2 H) (chemical shift relative to internal Me_4Si); MS (15 eV), *m/e* 502 (M^+), 334 (M^+ - 6CO). Anal. Calcd for $C_{20}Fe_2H_{26}N_2O_6$: C, 47.8; H, 5.18; N, 5.58. Found: C, 47.83; H, 5.29; N, 5.78.

Reaction of $CH_3C{\equiv}CN(C_2H_5)_2$ with $Fe_2(CO)_9$. 1-(Diethylamino)propyne (400 mg, 3.6 mmol) was added to a solution of $Fe_2(CO)_9$ (390 mg, 1.1 mmol) in 100 mL of THF. The solution was stirred at room temperature for 24 h. Chromatography as described above yielded $C_{20}Fe_2H_{26}N_2O_6$ (I, 180 mg, 46%), identified by its infrared spectrum.

---

[1] Muetterties, E. L. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 545.

[2] Astier, A.; Daran, J. C.; Jeannin, Y.; Rigault, C. *J. Organomet. Chem.* **1983**, *241*, 53.

[3] Ficini, J. *Tetrahedron* **1976**, *32*, 1449.

[4] King, R. B.; Harmon, C. A. *Inorg. Chem.* **1976**, *15*, 879.

[5] D'Angelo, J.; Ficini, J.; Martinon, S.; Riche, C.; Sevin, A. *J. Organomet. Chem.* **1979**, *177*, 265.

[6] Dötz, K. H. *Chem. Ber.* **1980**, *11B*, 3597.

[7] Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

0276-7333/84/2303-1158$01.50/0

Table I

	I	II	III
	A. Crystal Data		
formula	$Fe_2C_{20}H_{26}N_2O_6$	$(Ru_2C_{19}H_{26}N_2O_5)_2$ (disordered)	$(Ru_2C_{19}H_{26}N_2O_5)_2$
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
lattice const			
a, Å	16.001 (5)	14.135 (1)	8.059 (3)
b, Å	11.209 (1)	14.158 (1)	16.440 (9)
c, Å	13.550 (9)	10.696 (1)	16.05 (1)
β, deg	103.64 (7)	97.55 (1)	96.65 (6)
V, Å^3	2361	2122	2113
Z	4	2	2
mol wt	502.1	1129.1	1129.1
ρ(calcd), g cm^{-3}	1.41	1.77	1.77
μ, cm^{-1}	11.96	13.87	13.91
	B. Data Collection		
diffractometer	laboratory-made, automatic three-circle diffractometer		Philips PW 1100
radiatn	Mo Kα (λ = 0.710 69 Å)		Mo Kα (λ = 0.710 69)
monochromator	graphite monochromator set in front of the counter		graphite
scan range, deg	$3 < 2\theta < 46$	$3 < 2\theta < 46$	$4 < 2\theta < 45$
scan type	θ-2θ	θ-2θ	θ-2θ
scan speed, deg min^{-1}	1.9	1.9	0.6
scan width, deg	1.2 + 0.345 tan θ	1.0 + 0.345 tan θ	0.9 + 0.3 tan θ
reflctns independent	2658	2924	2510
reflctns obsd	1947	2403	1818
criterion	$F > 3\sigma(F)$	$F > 3\sigma(F)$	$F > 3\sigma(F)$
F(000)	1039.92	1127.96	1127.96
	C. Refinement of the Structures		
final no. of variables	295	288	297
$R = \Sigma\|(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.0653	0.0425	0.0681
$R_w = \{\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w(F_o)^2\}^{1/2}$	0.0655	0.041	0.0361
weighting scheme ($w = k/\|\sigma(F)\|^2$), k =	0.713	5.66	1.73

Reaction of $CH_3C{\equiv}CN(C_2H_5)_2$ with $Ru_3(CO)_{12}$. A solution of $Ru_3(CO)_{12}$ (90 mg, 0.14 mmol) and the aminoalkyne in large excess (240 mg, 2.2 mmol) in toluene was boiled under reflux for 6 h. A few brown crystals were isolated (II) after the solution was cooled at room temperature. Chromatography on silica gel column with petroleum ether/ethanol mixture eluted a yellow band. When the solution was cooled to 0 °C, yellow crystals were obtained (10 mg, 11%, III): IR ν(CO) 1990 (s), 1995 (s), 1910 (s), 1895 (s) cm^{-1}; MS (70 eV), m/e 1129 (M$^+$), 905 (M$^+$ − 8CO).

Spectral Studies. Infrared spectra (KBr pellets) were recorded on a Perkin-Elmer 597 spectrometer, ^{1}H NMR spectrum on a JEOL HA 60 spectrometer, and mass spectra on a AEI·MS30 spectrometer.

X-ray Studies. For each compound a survey of the X-ray diffraction pattern was made by precession techniques. Compounds I and II were set up on a laboratory-made, automatic three-circle diffractometer, and cell dimensions and orientation matrices were obtained by least-squares analysis from the setting angles of nine reflections. The scintillation counter was fitted with a pulse-height analyzer tuned to accept 90% of the Mo Kα peak. A takeoff angle of 3° was used. A Philips PW1100 diffractometer was used for compound III. The cell dimensions were refined by a least-squares best fit to 25 reflections.

Crystal data and data collection parameters are listed in Table I. For compounds I and II, two standard reflections were monitored every 100 reflections, whereas in III, three standards were measured every 2 h; no significant fluctuations were observed. The three-circle diffractometer was not fitted with attenuation filters, so if the counting rate exceeded 7000 counts s^{-1}, intensities for compounds I and II were corrected for counting losses. All data were corrected for Lorentz and polarization factors, but no absorption correction was applied.

Computations were performed by using the SHELX 76 system of computer programs[8] on the CII IRIS 80 computer. The analytical scattering factors for neutral iron, ruthenium, nitrogen, oxygen, carbon, and hydrogen were used throughout the analysis; both the real and imaginary components of anomalous dispersion were included for iron and ruthenium atoms.[9]

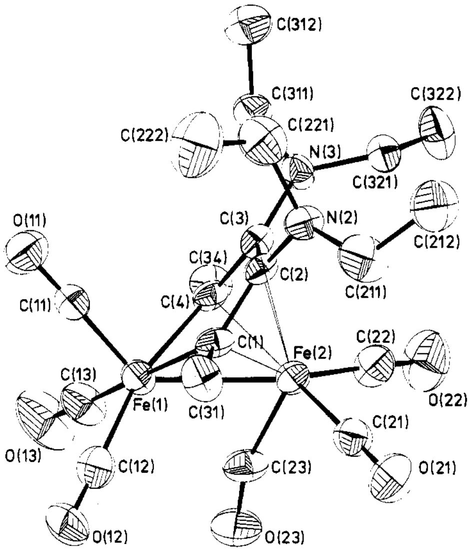

Figure 1. The $[Fe_2(CO)_6\{C_4(CH_3)_2[N(C_2H_5)_2]_2\}]$ molecule. Ellipsoids of 30% probability are shown.

All the structures were determined by the heavy-atom method using the Patterson function to locate the metal and Fourier syntheses to find all other non-hydrogen atoms. Refinements were by full-matrix least squares including isotropic and then anisotropic temperature factors. All refinements began with unit weights that were replaced in the final rounds of calculations by a weighting scheme of the form $w = k/[\sigma^2(F)]$. For the last cycles of refinement, hydrogen atoms were added in idealized positions but allowed to shift according to the movement of the parent C atoms and assigned a refineable overall isotropic thermal parameter. The criteria for a satisfactory completed analysis were the ratio of the parameter shifts to standard deviations all less than 0.4, and no significant features in the final difference map. Main features of the refinement appear in Table I, part C.

---

[8] Computer programs used were Sheldrick's SHELX 76, Johnson's ORTEP-2, and locally written routines.

[9] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. IV.

Table II. Fractional Atomic Coordinates of Compound I (with Esd's in Parentheses)

atom	*x/a*	*y/b*	*z/c*
Fe(1)	−0.2583 (1)	0.2345 (1)	0.2031 (1)
Fe(2)	−0.2158 (1)	0.0463 (1)	0.1278 (1)
C(1)	−0.3300 (6)	0.0844 (9)	0.1652 (7)
C(2)	−0.3016 (6)	−0.0175 (9)	0.2255 (6)
C(3)	−0.2158 (6)	−0.0012 (9)	0.2905 (7)
C(4)	−0.1767 (6)	0.1117 (9)	0.2777 (6)
C(31)	−0.4216 (7)	0.094 (1)	0.0995 (9)
C(34)	−0.0830 (7)	0.136 (1)	0.3266 (8)
N(2)	−0.3471 (6)	−0.1224 (8)	0.2295 (6)
N(3)	−0.1734 (5)	−0.0892 (7)	0.3550 (6)
C(211)	−0.389 (1)	−0.191 (1)	0.141 (1)
C(221)	−0.378 (1)	−0.136 (1)	0.327 (1)
C(212)	−0.387 (1)	−0.320 (1)	0.153 (1)
C(222)	−0.456 (1)	−0.074 (2)	0.331 (2)
C(311)	−0.1320 (7)	−0.057 (1)	0.4613 (7)
C(321)	−0.1703 (8)	−0.214 (1)	0.3239 (8)
C(312)	−0.171 (1)	−0.125 (1)	0.538 (1)
C(322)	−0.0803 (9)	−0.267 (1)	0.350 (1)
C(11)	−0.3102 (8)	0.251 (1)	0.2998 (9)
O(11)	−0.3500 (6)	0.2636 (9)	0.3633 (7)
C(12)	−0.3262 (9)	0.329 (1)	0.108 (1)
O(12)	−0.3675 (7)	0.3919 (8)	0.0490 (7)
C(13)	−0.1807 (9)	0.353 (1)	0.239 (1)
O(13)	−0.1339 (8)	0.4312 (9)	0.264 (1)
C(21)	−0.2723 (8)	−0.011 (1)	0.0077 (9)
O(21)	−0.3067 (7)	−0.0466 (9)	−0.0715 (7)
C(22)	−0.120 (1)	−0.036 (1)	0.1297 (9)
O(22)	−0.0573 (7)	−0.086 (1)	0.1289 (9)
C(23)	−0.1818 (8)	0.182 (1)	0.0781 (9)
O(23)	−0.1506 (7)	0.2480 (9)	0.0318 (7)

For each complex, copies of the observed structure amplitudes and structure factors calculated from the final atomic parameters are available. Atomic coordinates are given in Tables II and III and bond lengths and angles in Tables IV–VI.

Results and Discussion

Compound I. The unit cell contains four dinuclear molecules separated by van der Waals' distances. The dinuclear molecule, shown in Figure 1, is another example of the well-known metallacyclopentadiene complexes.[10-14]

The butadiene fragment results from the tail-to-tail coupling of two 1-(diethylamino)propyne molecules, with nitrogen atoms attached to the C(2) and C(3) carbon atoms. This situation is interesting when the trimerization of aminoalkynes catalyzed by Ni(II) or Ni(0) is considered. Ficini et al.[15] observed a benzene ring substituted by three amino groups in positions 1, 2, and 4, without any other isomers. This is consistent with a tail-to-tail coupling followed by a Diels–Alder attack of a third aminoalkyne molecule. A head-to-tail coupling would lead to a mixture of 1,2,4- and 1,3,5-isomers.[16]

The presence of the nitrogen atoms affects the overall geometry of the metallcyclopentadiene moiety π bonded to a second metal atom.

First of all, from the comparison of the bond lengths of Fe(2) to the ring (Table IV), it appears that the Fe(1)–C(1)–C(2)–C(3)–C(4) ring is bent around C(1)–C(4) making them very much like bridging carbenes. The electronic structure can be described by at least two mesomeric forms (Figure 2). The first one is a ferrole π bonded to another iron atom. The second one is based upon the keten-immonium ylide form of the aminoalkyne; both iron atoms appear identical. A symmetrical location of iron atoms with respect to the butadiene plane would give a distance of about 1.0 Å.

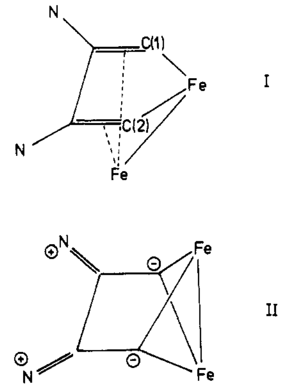

Figure 2. Two possible mesomeric structures for ferracyclopentadiene.

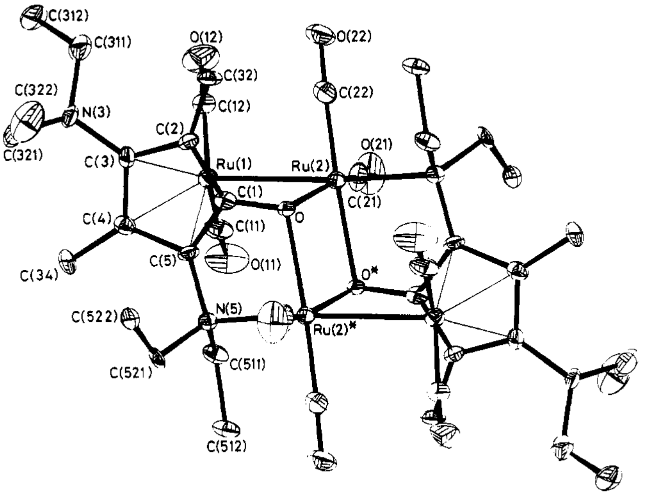

Figure 3. The $[Ru_4(CO)_8\{C_5O(CH_3)_2[N(C_2H_5)_2]_2\}_2]$ molecule. Ellipsoids of 36% probability are shown.

Our compound is in between these two forms since Fe(1) is above the butadiene plane by 0.43 (1) Å in contrast to 0.23 (1) Å in $\{(CO)_3Fe[C_4(C_6H_5)_4]\}Fe(CO)_3$[14] or 0.19 (1) Å found in $\{(CO)_2P(C_6H_5)_3Fe[C_4(C_6H_5)_4]\}Fe(CO)_3$.[13]

Secondly the Fe(2)–C(1) length is significantly shorter than Fe(2)–C(4), whereas the ring Fe–C distances are normal.[10-14] Moreover the CH_3 group attached to C(1) is 0.14 Å above the butadiene plane while the CH_3 attached to C(4) is 0.21 Å below this plane.

These facts may be related to the pπ(N)–pπ(ring) overlap that can be inferred from the C(2)–N(2) and C(3)–N(3) distances that are shorter than the C–N single bond (1.47 Å),[17] and from the sum of the angles around nitrogen which is very close to 360°. However this π interaction is not fully achieved since the dihedral angles between each of the N(2)–C(211)–C(221)–C(2) and N(3)–C(311)–C(321)–C(3) planes and the butadiene plane are 65° and 48°, respectively. The difference in both these angles might be responsible for the dissymetry observed between C(1) and C(4). Such a difference could be attributed to the crystal packing; as a matter of fact the ^1H NMR from a solution displays only a singlet at 2.25 ppm

---

(10) Hock, A. A.; Mills, O. S. *Acta Crystallogr.* **1969**, *14*, 139.

(11) Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 5068.

(12) Bennett, M. J.; Graham, W. A. G.; Smith, R. A.; Stewart, R. P., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 1684.

(13) Todd, L. J.; Hickey, J. P.; Wilkinson, J. R.; Huffman, J. C.; Folting, K. *J. Organomet. Chem.* **1976**, *112*, 167.

(14) Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2928.

(15) Ficini, J.; D'Angelo, J.; Falou, S. *Tetrahedron Lett.* **1977**, *19*, 1645.

(16) Whitesides, G. M.; Ehmann, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 3800.

(17) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1968; Vol. III.

Table III. Fractional Atomic Coordinates of Compounds II and III (with Esd's in Parentheses)[a]

atom	*x/a*	*y/b*	*z/c*	*B*(iso), Å^2
		A. Compound II		
Ru(1)	−0.13693 (5)	0.15330 (4)	0.12075 (6)	
Ru(2)	0.04190 (5)	0.07471 (4)	0.12487 (5)	
C(1)	−0.1336 (6)	−0.0038 (5)	0.0863 (7)	
C(2)	−0.1770 (6)	0.0134 (6)	0.1990 (8)	
C(3)	−0.2635 (6)	0.0658 (6)	0.1626 (8)	
C(4)	−0.2718 (6)	0.0850 (6)	0.0300 (8)	
C(5)	−0.1912 (6)	0.0422 (5)	−0.0157 (7)	
O	−0.0519 (4)	−0.0483 (3)	0.0780 (4)	
N(3)	−0.3321 (5)	0.0846 (6)	0.2420 (7)	
N(5)	−0.1724 (5)	0.0246 (5)	−0.1449 (6)	
C(32)	−0.1453 (8)	−0.0290 (7)	0.3274 (8)	
C(34)	−0.3574 (8)	0.1320 (7)	−0.042 (1)	
C(311)	−0.418 (1)	0.022 (1)	0.215 (2)	6.5 (2)
C(311)′	−0.365 (1)	−0.003 (1)	0.302 (2)	6.5 (2)
C(321)	−0.369 (2)	0.183 (1)	0.237 (2)	6.5 (2)
C(321)′	−0.320 (2)	0.155 (1)	0.343 (2)	6.5 (2)
C(312)	−0.468 (1)	−0.006 (2)	0.326 (2)	11.0 (4)
C(322)	−0.364 (2)	0.251 (1)	0.337 (2)	11.0 (4)
C(511)	−0.1541 (7)	0.1180 (6)	−0.2103 (8)	
C(512)	−0.146 (1)	0.1086 (7)	−0.3520 (8)	
C(521)	−0.2588 (7)	−0.0239 (7)	−0.2191 (9)	
C(522)	−0.3012 (8)	−0.1025 (7)	−0.145 (1)	
C(11)	−0.1148 (7)	0.2313 (7)	0.2644 (9)	
O(11)	−0.1045 (7)	0.2767 (6)	0.3532 (7)	
C(21)	0.0884 (7)	0.1957 (7)	0.1289 (8)	
O(21)	0.1136 (6)	0.2732 (5)	0.1339 (9)	
C(12)	−0.1262 (8)	0.2599 (6)	0.0214 (9)	
O(12)	−0.1247 (8)	0.3251 (5)	−0.0415 (7)	
C(22)	0.0426 (7)	0.0959 (6)	0.2934 (8)	
O(22)	0.0491 (6)	0.1110 (6)	0.4002 (6)	
		B. Compound III		
Ru(1)	−0.1048 (1)	0.02259 (7)	0.18898 (7)	
Ru(2)	−0.0921 (1)	0.08875 (6)	0.03287 (7)	
C(1)	0.129 (1)	−0.0059 (7)	0.1289 (9)	
C(2)	0.176 (1)	0.0376 (7)	0.2038 (8)	
C(3)	0.133 (1)	−0.0106 (8)	0.2725 (8)	
C(4)	0.050 (1)	−0.0827 (8)	0.2421 (8)	
C(5)	0.048 (1)	−0.0795 (8)	0.1499 (7)	
O	0.1421 (9)	0.0175 (4)	0.0499 (5)	
N(3)	0.174 (1)	0.0021 (7)	0.3602 (7)	
N(5)	0.014 (1)	−0.1438 (6)	0.0889 (6)	
C(32)	0.287 (2)	0.1137 (7)	0.2057 (8)	
C(34)	−0.004 (2)	−0.1515 (8)	0.2944 (8)	
C(311)	0.179 (2)	0.083 (1)	0.390 (1)	
C(312)	0.108 (2)	0.0962 (9)	0.4716 (9)	
C(321)	0.295 (3)	−0.051 (1)	0.402 (1)	
C(322)	0.473 (2)	−0.043 (1)	0.375 (1)	
C(511)	−0.169 (2)	−0.1660 (8)	0.0786 (9)	
C(512)	−0.214 (2)	−0.2419 (7)	0.0256 (9)	
C(521)	0.120 (2)	−0.2174 (7)	0.1156 (9)	
C(522)	0.298 (2)	−0.1982 (8)	0.1519 (8)	
C(11)	−0.186 (2)	0.1081 (8)	0.2478 (9)	
O(11)	−0.242 (1)	0.1590 (7)	0.2854 (7)	
C(12)	−0.325 (2)	−0.0167 (8)	0.1693 (9)	
O(12)	−0.460 (1)	−0.0377 (7)	0.1558 (7)	
C(21)	−0.312 (2)	0.1158 (9)	0.0331 (8)	
O(21)	−0.450 (1)	0.1329 (7)	0.0363 (7)	
C(22)	−0.058 (2)	0.1788 (8)	0.0968 (9)	
O(22)	−0.040 (1)	0.2391 (6)	0.1355 (6)	

[a] The prime refers to C atoms of the ethyl groups in statistical distribution.

for the methyl groups attached to C(1) and C(4), which then are identical.

Compounds II and III. The crystal structure of compounds II and III consists of discrete tetranuclear molecules separated by van der Waals distances. A view of the molecule is shown in Figure 3. The geometry presents several interesting features: head-to-tail coupling of the aminoalkyne instead of tail-to-tail, four metallic centers in two units, a ketone group doubly bonded by the two lone pairs of its oxygen, and only one of the two nitrogen atoms coordinated.

The whole molecule has an inversion center that relates two dimetallic subunits containing a metal–metal bond. These subunits are connected to each other by a double oxygen bridge; these oxygen atoms belong to ketone groups. Both independent ruthenium atoms exhibit different surroundings: that of Ru(1) may be considered as tetrahedral with one vertex occupied by a cyclopentadiene ring and the three others occupied by two CO groups and Ru(2), in a piano stool like arrangement. That of Ru(2) is octahedral with two CO groups in cis positions, each trans to a bridging oxygen atom; the last two trans vertices are occupied by one nitrogen atom and the Ru(1) atom.

It is worthwhile to note that compounds II and III are identical, but both ethyl groups attached to N(3) are disordered in compound II. The disorder can be described

Table IV. Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for Compound I

Bond Distances

Fe(1)-C(11)	1.719 (14)	N(2)-C(211)	1.447 (16)	C(1)-C(31)	1.528 (13)
Fe(1)-C(12)	1.823 (12)	N(2)-C(221)	1.524 (20)	C(4)-C(34)	1.514 (14)
Fe(1)-C(13)	1.806 (13)	N(3)-C(311)	1.481 (11)	C(2)-N(2)	1.391 (13)
Fe(2)-C(21)	1.786 (12)	N(3)-C(321)	1.466 (13)	C(3)-N(3)	1.385 (12)
Fe(2)-C(22)	1.783 (15)	Fe(1)-C(1)	2.033 (10)	C(211)-C(212)	1.463 (20)
Fe(2)-C(23)	1.802 (13)	Fe(1)-C(4)	2.000 (10)	C(221)-C(222)	1.439 (28)
C(11)-O(11)	1.193 (17)	Fe(2)-C(1)	2.052 (10)	C(311)-C(312)	1.538 (20)
C(12)-O(12)	1.145 (15)	Fe(2)-C(2)	2.236 (10)	C(321)-C(322)	1.519 (18)
C(13)-O(13)	1.150 (17)	Fe(2)-C(3)	2.268 (10)	Fe(1)-Fe(2)	2.506 (2)
C(21)-O(21)	1.153 (15)	Fe(2)-C(4)	2.110 (9)	Fe(2)-C(13)	2.386 (8)
C(22)-O(22)	1.151 (20)	C(1)-C(2)	1.415 (13)		
C(23)-O(23)	1.154 (17)	C(2)-C(3)	1.457 (12)		
		C(3)-C(4)	1.441 (14)		

Bond Angles

C(11)-Fe(1)-C(12)	99.4 (6)	C(1)-C(2)-C(3)	112.1 (8)	Fe(2)-C(21)-O(21)	177.6 (13)
C(11)-Fe(1)-C(13)	98.1 (6)	C(1)-C(2)-N(2)	127.2 (8)	Fe(2)-C(22)-O(22)	177.6 (14)
C(11)-Fe(1)-C(1)	86.5 (5)	C(3)-C(2)-N(2)	120.6 (8)	Fe(2)-C(23)-O(23)	161.9 (12)
C(11)-Fe(1)-C(4)	93.8 (5)	C(2)-N(2)-C(211)	124.0 (9)	Fe(1)-C(4)-C(3)	114.5 (7)
C(12)-Fe(1)-C(13)	91.1 (6)	C(2)-N(2)-C(221)	113.5 (9)	Fe(1)-C(4)-C(34)	124.0 (7)
C(12)-Fe(1)-C(1)	95.5 (5)	C(211)-N(2)-C(221)	119.0 (11)	C(3)-C(4)-C(34)	121.3 (8)
C(12)-Fe(1)-C(4)	165.7 (5)	N(2)-C(211)-C(212)	116.1 (11)	C(4)-C(3)-C(2)	114.3 (8)
C(13)-Fe(1)-C(1)	171.3 (5)	N(2)-C(221)-C(222)	116.4 (14)	C(4)-C(3)-N(3)	122.6 (8)
C(13)-Fe(1)-C(4)	92.6 (5)	C(21)-Fe(2)-C(22)	94.3 (6)	C(2)-C(3)-N(3)	123.0 (9)
C(1)-Fe(1)-C(4)	79.7 (4)	C(21)-Fe(2)-C(23)	95.6 (5)	C(3)-N(3)-C(311)	118.7 (8)
Fe(1)-C(1)-C(2)	115.9 (6)	C(22)-Fe(2)-C(23)	96.2 (6)	C(3)-N(3)-C(321)	122.9 (8)
Fe(1)-C(1)-C(31)	119.8 (7)	Fe(1)-C(11)-O(11)	176.7 (10)	C(311)-N(3)-C(321)	118.4 (8)
C(2)-C(1)-C(31)	121.7 (9)	Fe(1)-C(12)-O(12)	177.8 (11)	N(3)-C(311)-C(312)	112.3 (9)
		Fe(1)-C(13)-O(13)	176.8 (14)	N(3)-C(321)-C(322)	113.6 (9)

Table V. Bond Distances (Å) with Esd's in Parentheses for Compound III[a]

Ru(1)-C(11)	1.854 (14)	Ru(2)-C(21)	1.83 (2)
Ru(1)-C(12)	1.884 (14)	Ru(2)-C(22)	1.80 (1)
Ru(1)-C(1)	2.265 (12)	Ru(2)-O	2.211 (7)
Ru(1)-C(2)	2.264 (13)	Ru(2)-O*	2.204 (7)
Ru(1)-C(3)	2.272 (12)	Ru(2)-N(5)	2.31 (1)
Ru(1)-C(4)	2.243 (13)		
Ru(1)-C(5)	2.216 (13)	C(21)-O(21)	1.15 (2)
		C(22)-O(22)	1.18 (2)
C(11)-O(11)	1.15 (2)		
C(12)-O(12)	1.13 (2)	C(5)-N(5)	1.44 (2)
		N(5)-C(511)	1.52 (2)
C(1)-C(2)	1.41 (2)	N(5)-C(521)	1.51 (2)
C(2)-C(3)	1.43 (2)	C(511)-C(512)	1.54 (2)
C(3)-C(4)	1.42 (2)	C(521)-C(522)	1.52 (2)
C(4)-C(5)	1.48 (2)		
C(5)-C(1)	1.43 (2)	C(3)-N(3)	1.43 (2)
C(1)-O	1.34 (2)	N(3)-C(311)	1.42 (2)
C(2)-C(32)	1.54 (2)	N(3)-C(321)	1.43 (2)
C(4)-C(34)	1.50 (2)	C(312)-C(311)	1.50 (2)
		C(322)-C(321)	1.56 (3)
Ru(1)-Ru(2)	2.744 (2)		
Ru(2)-Ru(2)*	3.492 (2)		

[a] The asterisk refers to atoms related by the inversion center.

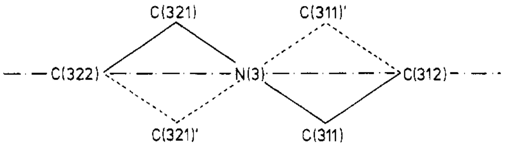

Figure 4. Scheme of the disordered ethyl groups.

as a statistical distribution of each CH_2 group on two sites related by a plane containing C(3), N(3), and both terminal methyl groups (Figure 4). Only bond distances and angles of compound III appear in Tables V and VI.

An interesting feature of this structure is the formation of a cyclopentadienone that results from the head-to-tail coupling of two molecules of aminoalkyne and the insertion of one CO molecule. (Cyclopentadienone)metal complexes are among the products commonly isolated from reactions of acetylenes with metal carbonyls; however, X-ray structural determinations mostly refer to iron[18-21] or cobalt[22] complexes. These structures always show that the ketone group is out of the plane of the butadiene system. However, in our compound, the ketone group is in the butadiene plane, suggesting that the C_5 ring is a cyclopentadiene ring; this is also supported by the fact that the five carbon–carbon bond lengths of the ring are all identical within the standard deviations and also that the distances from Ru(1) to the carbon atoms of the ring are all identical and are in the range of the values usually observed in ruthenium cyclopentadiene complexes,[23,24] 2.21–2.27 Å. These structural results suggest that the electronic structure of that ring is analogous to a phenolate. The low carbonyl stretching frequency, 1470 cm^{-1}, of the CO bond supports this view. Moreover, the C–O bond length is 1.34 (2) Å instead of the 1.20 Å expected for ketones.[25,26] One might infer from this that the presence of nitrogen as an electron-donating substituent on the ring favors resonance over the ring. In support of this point one should note that the sum of the angles around N(3) is 350 (2)° and also that the dihedral angle between the plane defined by N(3) and both CH_2 groups and the plane of the C_5 ring is 62°, close to the 65° observed in the iron complex. This would be responsible for the transformation of the ketone into a

---

(18) Bailey, N. A.; Mason, R. *Acta Crystallogr.* **1966**, *21*, 652.
(19) Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1977**, *128*, 237.
(20) Jens, K. J.; Weiss, E. *J. Organomet. Chem.* **1981**, *210*, C27.
(21) Cash, G. C.; Pettersen, R. C. *Inorg. Chem.* **1978**, *17*, 650.
(22) Clearfield, A.; Rudolf, P.; Bernal, I.; Rausch, M. D. *Inorg. Chim. Acta* **1980**, *42*, 17.
(23) Takusagawa, F.; Koetzle, T. F. *Am. Cryst. Assoc.*, Ser. 2, **1980**, *7*, 16.
(24) Killops, S. D.; Knox, S. A. R.; Riding, G. H.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1978**, 486.
(25) Dubourg, A.; Roques, R.; Guy, E. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2938.
(26) Kaftory, M. *Acta Crystallogr., Sect. B.* **1980**, *B36*, 597.

Table VI. Bond Angles (deg) with Esd's in Parentheses for Compound III[a]

C(11)-Ru(1)-C(12)	87.7 (6)	C(21)-Ru(2)-C(22)	83.2 (6)	C(311)-N(3)-C(321)	116.2 (12)
C(11)-Ru(1)-Ru(2)	102.7 (4)	O-C(1)-C(2)	128.0 (11)	C(3)-N(3)-C(311)	117.5 (11)
C(12)-Ru(1)-Ru(2)	96.8 (4)	O-C(1)-C(5)	123.3 (11)	C(3)-N(3)-C(321)	116.0 (12)
O-Ru(2)-Ru(1)	78.4 (2)	C(2)-C(1)-C(5)	108.4 (11)	N(3)-C(311)-C(312)	114.9 (14)
O-Ru(2)-O*	75.5 (3)	C(1)-C(2)-C(3)	107.9 (11)	N(3)-C(321)-C(322)	114.2 (15)
O-Ru(2)-N*	90.1 (3)	C(2)-C(3)-C(4)	110.3 (11)	C(5)-N(5)-Ru(2)*	103.7 (7)
O-Ru(2)-C(21)	160.5 (5)	C(3)-C(4)-C(5)	105.2 (11)	C(5)-N(5)-C(511)	110.4 (9)
O-Ru(2)-C(22)	107.1 (5)	C(4)-C(5)-C(1)	108.1 (11)	C(5)-N(5)-C(521)	110.1 (9)
Ru(1)-Ru(2)-O*	102.3 (2)	C(1)-C(2)-C(32)	121.9 (11)	Ru(2)*-N(5)-C(511)	111.7 (7)
Ru(1)-Ru(2)-N(5)*	166.5 (2)	C(3)-C(2)-C(32)	129.0 (11)	Ru(2)*-N(5)-C(521)	110.8 (8)
Ru(1)-Ru(2)-C(21)	87.4 (5)	C(2)-C(3)-N(3)	129.0 (11)	C(511)-N(5)-C(521)	110.0 (9)
Ru(1)-Ru(2)-C(22)	80.1 (5)	C(4)-C(3)-N(3)	120.5 (11)	N(5)-C(511)-C(512)	114.4 (11)
O*-Ru(2)-N(5)*	81.3 (3)	C(3)-C(4)-C(34)	126.6 (11)	N(5)-C(521)-C(522)	114.3 (10)
O*-Ru(2)-C(21)	94.9 (5)	C(5)-C(4)-C(34)	127.8 (11)	C(1)-O-Ru(2)	96.5 (6)
O*-Ru(2)-C(22)	176.9 (5)	C(4)-C(5)-N(5)	129.1 (11)	C(1)-O-Ru(2)*	108.3 (7)
N*-Ru(2)-C(21)	105.4 (5)	C(1)-C(5)-N(5)	121.1 (11)	Ru(2)-O-Ru(2)*	105.4 (3)
N*-Ru(2)-C(22)	96.8 (5)				

[a] See footnote *a* in Table V.

tertiary alcohol. In conclusion, the ring could be described as a cyclopentadienol.

Another interesting point is the peculiar complexing mode of this compound. The cyclopentadienol group behaves as a pentadentate ligand: the ring is twice π bonded to Ru(1), the oxygen bridges the ruthenium Ru(2) and its symmetrical Ru(2)*, and the nitrogen N(5) is σ bonded to Ru(2)*. To the best of our knowledge, there is one example of the oxygen of a cyclopentadienone group bridging two metal atoms by its two lone pairs: it is a compound involving silver atoms;[27] and the three-coordinate oxygen has a planar geometry with the sum of the angles around oxygen equal to 360°. In our case the sum of the angles around oxygen, 308°, shows that oxygen has a pyramidal geometry. This means that this oxygen is actually not sp^2. This supports again the view that this oxygen has very likely some residual electron density on it; namely, it seems better to consider it as an olato group.

Owing to this geometry, this oxygen is at the apex of a pyramid, the three faces of which are the planes O(1)–C(1)–Ru(1)–Ru(2), O(1)–Ru(2)–Ru(2)*–O(1)*, and O(1)–Ru(2)*–N(5)–C(5)–C(1). The plane O(1)–Ru(2)–Ru(2)* contains the inversion center of the molecule; thus the two oxo bridges are in the same plane and they are symmetrical. The Ru(2)-Ru(2)* distance equal to 3.492 (2) Å is too long to be regarded as a metal–metal bond. The electron bookkeeping leads to 17 electrons on each independent metal, Ru(1) and Ru(2); the 18-electron configuration is achieved by the Ru(1)–Ru(2) bond as can be inferred from the 2.744 (1) Å bond length. This dimetallic group is linked by Ru(1) to the cyclopentadiene and by Ru(2) to the oxygen; the four atoms Ru(1), Ru(2), O(1), and C(1) are in the same plane. This plane, its symmetry-related plane (with respect to the inversion center), and the plane containing the two oxo bridges have a chairlike arrangement.

The last point to be discussed deals with the two different coupling modes of the aminoalkyne, symmetrical in the ferracyclopentadiene complex and asymmetrical in the (cyclopentadienolato)ruthenium complex. The formation of cyclopentadienone from an unsymmetric alkyne, $RC{\equiv}CR'$, may lead to three isomers; however, it is known that the coupling often occurs in a stereoselective way. One of the suggested factors inducing the formation of the head-to-tail isomer (2,4-isomer) is the difference in electronegativities of R and R′.[21] In the case of metallacycles that result from the coupling of unsymmetrical alkynes, the structural results are scanty; it seems, however, that symmetric coupling most frequently occurs.[28] Although differences in the electronegativities of the aminoalkyne substituents would strongly suggest an unsymmetrical head-to-tail coupling, the ferracyclopentadiene described here results from a symmetrical tail-to-tail coupling, and it is worthwhile pointing out that a similar ruthenacyclopentadiene was obtained from the reaction of $Ru_3(CO)_{12}$ with the 1-(diethylamino)propyne.[29]

Two different mechanisms obviously have to be considered to explain these different coupling modes; they will be treated in a forthcoming paper.

Registry No. I, 90414-56-5; II, III, 90414-57-6; $CH_3C{\equiv}CN(C_2H_5)_2$, 4231-35-0; $Fe_3(CO)_{12}$, 17685-52-8; $Fe_2(CO)_9$, 15321-51-4; $Ru_3(CO)_{12}$, 15243-33-1; Fe, 7439-89-6; Ru, 7440-18-8.

Supplementary Material Available: Tables of anisotropic temperature factors, important least-squares planes, and observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

---

[27] Baker, P. K.; Broadley, K.; Connelly, N. G.; Kelly, B. A.; Kitchen, M. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, *9*, 1710.

[28] Chappel, S. D.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 739.

[29] Further details regarding this structure will not be included here because the compound looks identical as far as NMR, IR, and MS are concerned; a preliminary survey of single crystals shows isomorphism with the iron compound.