Ruthenium Carbonyl 1,4-Diaza-1,3-butadiene (R-DAB) Complexes*. Reactivity of $Ru_2(CO)_6$(R-DAB) Towards Hetero-allenes L (L = Carbodiimide, Sulphine), Resulting in C–C Bond Formation. X-ray Molecular Structure of $Ru_2(CO)_5$(t-BuN=CHC(H)(N-t-Bu)C(N-*p*-Tol)=N-*p*-Tol) and of $Ru_2(CO)_5$(i-PrN=CHC(H)(N-i-Pr)C(S)$C_{12}H_8$)

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Received December 7, 1984

Abstract

$Ru_2(CO)_6$(R-DAB)(R-DAB = 1,4-disubstituted-1,4-diaza-1,3-butadiene = RN=CH–CH=NR) (R-DAB stands for RN=CH–CH=NR: DAB = 1,4-*diaza*-1,3-*b*utadiene, see ref. 1) reacts with hetero-allenes L (L = carbodiimide = R′N=C=NR′, R′ = *p*-Tol, i-Pr, c-Hex, R = t-Bu; L = thiofluorenone-S-oxide = $C_{12}H_8C$=S=O, R = i-Pr, t-Bu, c-Hex) to yield C(R-DAB)–C(L) coupled products. From the reaction of $Ru_2(CO)_6$(t-Bu-DAB) with R′N=C=NR′, $Ru_2(CO)_5$(t-BuN=CHC(H)(Nt-Bu)C(NR′)=NR′)($Ru_2(CO)_5$(AIP{t-Bu, R′}), AIP = 1,2-di-*a*mino-2,3-di-*i*mino-*p*ropane) is obtained. The AIP-moiety is bonded to the two Ru-atoms via three of the four N-atoms, while the R′N-imine atom is not coordinated. This was proven by an X-ray crystal structure determination for R′ = *p*-Tol.

Crystals of $Ru_2(CO)_5$(AIP{t-Bu, *p*-Tol}) are triclinic, space group $P\bar{1}$ and cell constants: a = 16.69(2), b = 19.65(2) and c = 12.46(2) Å, α = 102.83(6), β = 108.24 and γ = 64.53(10)°; Z = 4.6546. Reflections were used in the refinement, resulting in a final R = 0.056.

There are two independent molecules in the unit cell, having only slightly different geometries. The single Ru(1)–Ru(2) bond of 2.779(1) Å (mean) (throughout this paper, standard deviations of mean values are calculated by $\sigma = \{\chi_i(\chi_i - \chi)^2/N(N-1)\}^{1/2}$) is spanned by a slightly asymmetrically bridging carbonyl group (C(3)O(3)). Each Ru-atom is coordinated by two terminal CO-groups. The organic t-Bu-N(1)=C(6)–C(7)(t-BuN(2))–C(8)(*p*-Tol-N(4))=*p*-Tol-N(3) fragment is σ-N bonded via N(1) to Ru(2) while the amino N(2)- and N(4)-atoms are both symmetrically bridging the Ru(1)–Ru(2) bond. N(3) is in a non-bonding position with respect to both Ru-atoms. The intra-ligand bond distances are in accord with a reduction of one imine bond of the former t-Bu-DAB ligand: C(7)–N(2) = 1.50(1) Å (mean). The new C(7)–C(8) bond has a bond length of 1.53(1) Å (mean).

During the reaction of $Ru_2(CO)_6$(R-DAB) with the sulphine $C_{12}H_8C$=S=O, CO_2 gas evolved and the product, *i.e.* $Ru_2(CO)_5$(RN=CHC(H)(NR)C(S)$C_{12}H_8$) no longer contains the sulphine's oxygen, as was proven by an X-ray crystal structure determination for R = i-Pr.

Crystals of $Ru_2(CO)_5$(i-PrN=CHC(H)(N-i-Pr)C(S)-$C_{12}H_8$) are orthorhombic, space group $P2_12_12_1$ and cell constants: a = 14.822(5), b = 16.951(28) and c = 25.413(16) Å; Z = 8.1304. Reflections were used in the refinement, resulting in a final R = 0.047.

There are two independent molecules in the unit cell having non-significant differences in geometry. The single Ru(1)–Ru(2) bond of 2.811(1) Å (mean) is bridged by one carbonyl group (C(22)O(1)). Furthermore, each Ru-atom is coordinated by two terminal CO groups. The organic i-Pr(N(2)=C(2)–C(1)(i-PrN(1))–C(3)–(S)$C_{12}H_8$ moiety is σ-N(2) bonded to Ru(2). The N(1) symmetrically bridges the Ru(1)–Ru(2) bond, while S does so asymmetrically: Ru(1)–S = 2.43(1), Ru(2)–S = 2.54(1) Å (mean).

All complexes were characterized by IR-, FD-mass- and ^{1}H NMR-spectroscopy.

Introduction

1,4-Disubstituted-1,4-diaza-1,3-butadienes (R-DAB = RN=CH–CH=NR) react with $Ru_3(CO)_{12}$ in a reaction sequence that is now known in great

*Part VII; for earlier parts: references 2–5.

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0020-1693/85/$3.30

detail [1, 2]. After the synthesis and characterization of all new reaction-intermediates, attention is now especially focused on the study of their reactivity. It has been observed that some polynuclear intermediates, *e.g.* $Ru_2(CO)_n$(R-DAB)(n = 5, 6) and $Ru_3(CO)_8$(R-DAB), are very reactive towards small ligands L, such as H_2, CH_2N_2, CO, acetylenes, olefines, allenes and R-DAB itself [2–5]. In some instances, R-DAB and L are found to be C–C-coupled in the reaction product. For this latter type of reactivity there seems to be two prerequisites. Firstly, the incoming ligand L must be able to add to a metal. Secondly η^2-C=N coordination of the R-DAB ligand facilitates reaction between R-DAB and L. Thus according to the first prerequisite it has been argued that the reactivity of $Ru_3(CO)_8$(R-DAB) towards CO and CH_2N_2 is due to the presence of one Ru-atom that has a gap in its coordination sphere [2]. The compound $Ru_2(CO)_5$(R-DAB), which only differs from $Ru_3(CO)_8$(R-DAB) in having a μ-CO group instead of an isolobal μ-Ru(CO)$_4$-moiety, reacts analogously (like an unsaturated complex) with various Lewis bases [3]. Earlier we described the reaction of $Ru_2(CO)_5$(R-DAB) with R-DAB, yielding $Ru_2(CO)_5$(R-IAE) (R-IAE = bis{R-imino-R-amino-ethane}, see Fig. 1), and we suggested that the C–C coupling reaction only occurred after prior coordination of the incoming R-DAB ligand [3, 4].

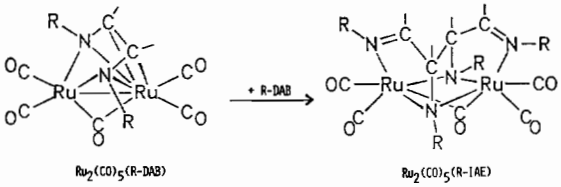


Fig. 1. The formation reaction of $Ru_2(CO)_5$(R-IAE).

From the reaction of $Ru_2(CO)_6$(R-DAB) with monosubstituted acetylenes, analogous C–C coupled products have been obtained. These have been found to be good precursors for catalytic species that promote the regiospecific trimerization of acetylenes, leading to 1,3,5-trisubstituted benzenes [5]. C–C coupling reactions on Ru_2-centres, linking alkynes with CO, olefines or carbenes, have also been investigated [6].

C–C bond formation between an unsaturated ligand and a substrate is of particular interest because of its possible relation to the carbon chain growth on a metal surface in heterogeneous catalysis [7]. Frequently, multisite coordination of such a ligand is one of the reasons for its activation and novel reactivity [8]. Accordingly, it has been argued that the C–C bond formation between R-DAB and another ligand in our R-DAB chemistry may occur because the α-diimine ligand is strongly activated by η^2-C=N coordination (compare the second prerequisite, vide supra). As a continuation of our study into the scope of this type of C–C bond formation reaction, we now report the reactivity of $Ru_2(CO)_6$–R-DAB towards some hetero-allenes L (L = R′N=C=NR′, $C_{12}H_8C$=S=O), yielding C(R-DAB)–C(L) coupled products.

Experimental

Materials and Apparatus

^{1}H NMR spectra were obtained on a Varian T60 and a Bruker WM 250 spectrometer. IR spectra were recorded with a Perkin–Elmer 283 spectrophotometer using a liquid cell (NaCl, 0.1 mm) or a gas cell (NaCl, 10 cm). Field Desorption (FD) mass spectra were obtained with a Varian MAT 711 double focusing mass spectrometer with a combined EI/FI/FD ion source, coupled to a spectro-system MAT-100 data acquisition unit. Tungsten wire (10 μm) FD-emitters containing carbon microneedles with an average length of 30 μm were used. The samples were dissolved in diethyl ether or toluene and then loaded onto the emitters using a dipping technique. An emitter current of 0–10 mA was used to desorb the samples. The ion source temperature generally was 70 °C [9].

Elemental analyses were obtained from the Elemental Analysis section of the Institute for Applied Chemistry, TNO, The Netherlands. All preparations were done in an atmosphere of purified nitrogen, using carefully dried solvents. The $Ru_2(CO)_6$(R-DAB) (R = i-Pr, c-Hex, t-Bu) [4] and the sulphine thiofluorenone-S-oxide ($C_{12}H_8C$=S=O) starting materials were prepared according to published methods [10]. The carbodiimides R′N=C=NR′ (R′ = *p*-Tol, i-Pr, c-Hex) were purchased from Aldrich and were used without purification. Silicagel (60 Mesh) for column chromatography was dried and activated before use.

Synthesis of $Ru_2(CO)_5$(t-BuN=CHC(H)(N-t-Bu)C(NR′)=NR′)

($Ru_2(CO)_5$(AIP{t-Bu, R′}), AIP = 1,2-diamino-2, 3-diimino-propane; R′ = *p*-Tol, i-Pr, c-Hex).

$Ru_2(CO)_6$(t-Bu-DAB) (0.5 mmol, prepared *in situ*) [3, 4] and 0.8 mmol of R′N=C=NR′ (R′ = *p*-Tol, i-pr, c-Hex) were refluxed in 40 ml of heptane or toluene until all IR-ν(CO) peaks due to the starting complex had disappeared, which took about 4–6 h. The solvent was evaporated *in vacuo* at 60 °C and the reaction mixture was purified by column chromatography (silica). Elution with hexane/ether (4/1) yielded unreacted starting materials. Subsequent elution with dichloromethane/ether (1/1) yielded a yellowish fraction which was collected. The solvent was evaporated *in vacuo* and the residue was dissolved in ether/hexane (1/2). Crystallization at –80 °C

yielded yellow crystals (60% yield, R′ = *p*-Tol) or a yellow precipitate (30%, yield, R′ = i-Pr < 10% yield, R′ = c-Hex) which was identified as $Ru_2(CO)_5$(AIP{t-Bu, R′}) by elemental analyses, FD-mass-, ^{1}H NMR-, and IR-spectroscopy and by a crystal structure determination for the R′ = *p*-Tol derivative (*vide infra*). Elution of the reaction mixture with dichloromethane afforded the already known complex $Ru_2(CO)_5$(t-Bu-IAE) [4, 5], in yields ranging from 30% (R′ = c-Hex) to less than 5% (R′ = *p*-Tol).

Synthesis of $Ru_2(CO)_5$(RN=CHC(H)(NR)C(S)$C_{12}H_8$) (R = i-Pr, t-Bu, c-Hex)

$Ru_2(CO)_6$(R-DAB) (R = i-Pr, t-Bu, c-Hex; 0.5 mmol, prepared *in situ*) and 0.8 mmol of the sulphine thiofluorenone-S-oxide ($C_{12}H_8C$=S=O) were stirred at 90 °C in 30 ml of toluene until all IR-ν(CO) peaks of the starting complex had disappeared. This took about 4 h. During the reaction CO_2 gas evolved, detected by IR-spectroscopy using a gas cell (Q- and R-branches, centred around 2344 cm^{-1}, were clearly resolved). The solvent was evaporated *in vacuo* and the reaction mixture was purified by column chromatography (silica; eluent: ether/hexane = 2/1). A yellow fraction was obtained, the solvent was evaporated *in vacuo* and the residue was recrystallized from ether/hexane (1/1), yielding 40% (based on Ru) of yellow crystals which were identified as $Ru_2(CO)_5$(RN=CHC(H)(NR)C(S)$C_{12}H_8$) by elemental analyses FD-mass- ^{1}H NMR- an IR-spectroscopy and by an X-ray crystal structure determination for the R = i-Pr derivative.

Crystal Structure Determination of $Ru_2(CO)_5$(AIP{t-Bu, p-Tol}) (Pentacarbonyl[1-para-tolylamino-1-para-tolylimino-2-tertiary-butylamino-3-tertiary-butyl-imino-propane]diruthenium: $C_{30}H_{34}N_4O_5Ru_2$)

Crystals of the title compound were triclinic, space group $P\bar{1}$. The unit cell had the dimensions: a = 16.69(2), b = 19.65(2) and c = 12.46(2) Å, α = 102.83(6), β = 108.24(6) and γ = 64.53(10)°; Z = 4, V = 3548.3 Å^3, d_c = 1.43 g cm^{-3}. Because of rapid disintegration of the crystals in air, one crystal was selected in a N_2-glove-box and sealed in a capillary under nitrogen. A total of 11,139 reflections with $\theta < 23°$ were measured on a NONIUS CAD 4 diffractometer using graphite monochromated Mo-K_α radiation. 6546 of these reflections ($-22 \leqslant h \leqslant 22$, $-27 \leqslant k \leqslant 26$,$0 \leqslant l \leqslant 13$) had intensities above the $2.5\sigma(I)$ level and the remaining reflections were treated as unobserved. No absorption correction was applied (μ = 8.75 cm^{-1}).

The positions of the four Ru-atoms in the asymmetric unit were derived from an E^2-Patterson synthesis. Subsequent F_o-syntheses revealed the remaining non-hydrogen atoms of the complex and the presence of diethyl ether. The ether atoms were not well-defined and were included in the anisotropic block-diagonal least-squares refinement with variable population parameters for two partial molecules. This converged to R = 0.062, but the parameters for the ether atoms were very unsatisfactory. Since the ether was of no direct interest, attempts to find a satisfactory model for it were abandoned. The refinement was continued with observed structure factors from which the ether contributions had been subtracted. These contributions were obtained by direct Fourier inversion of the corresponding electron density and had to be recalculated several times because of changes in the scale factor. This procedure converged to R = 0.056. The final electron count for the ether molecule was 35.9, implying a population parameter of 0.8. The anomalous dispersion of Ru was taken into account and a weighting scheme of $w = 1/(3.6 + F_o + 0.0053F_o^2)$ was applied (R_w = 0.087). No extinction correction was applied. The computer programs used for plotting, the scattering factors and dispersion correction were taken from the literature [11].

The molecular geometry of $Ru_2(CO)_5$(AIP{t-Bu, *p*-Tol}) (molecule B) with the numbering of the atoms is shown in Fig. 2, which is a PLUTO-drawing of the molecule. Atomic parameters and selected bond lengths and angles are given in Tables I and II, respectively.*

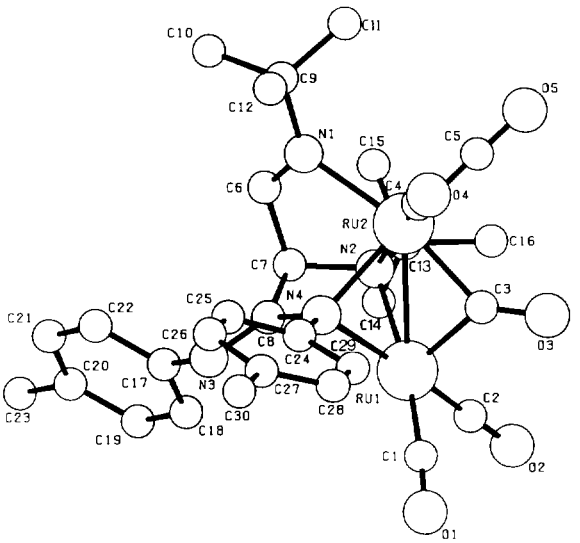


Fig. 2. The molecular geometry of $Ru_2(CO)_5$(AIP{t-Bu, *p*-Tol}).

*All bond lengths and angles, anisotropic thermal parameters, a list of calculated hydrogen-atoms coordinates and a list of observed and calculated structure factors have been deposited with the Cambridge Crystallographic Centre.

TABLE I. The Atomic Coordinates of $Ru_2(CO)_5$(AIP {t-Bu, *p*-Tol}) (e.s.d.).

Atom	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
Ru1	0.26076(9)	0.26280(7)	0.10060(9)	0.71245(5)	0.15758(4)	0.90264(6)
Ru2	0.24499(6)	0.21031(5)	0.27907(8)	0.74377(5)	0.28720(4)	0.95182(6)
N1	0.3435(6)	0.2055(5)	0.4410(7)	0.7674(6)	0.3282(5)	0.8163(7)
N2	0.3609(7)	0.1873(5)	0.2211(8)	0.8089(5)	0.1813(4)	0.8618(6)
N3	0.3552(6)	0.3739(5)	0.3210(8)	0.6205(5)	0.2097(5)	0.6217(6)
N4	0.2495(6)	0.3182(5)	0.2711(8)	0.6398(5)	0.2592(4)	0.8161(6)
O1	0.1388(14)	0.3943(11)	−0.0349(14)	0.5534(6)	0.1304(6)	0.9235(9)
O2	0.3045(14)	0.1917(12)	−0.1224(12)	0.8200(6)	0.0043(4)	0.9984(8)
O3	0.1133(9)	0.2095(9)	0.0455(11)	0.7364(6)	0.2177(5)	1.1430(6)
O4	0.0683(7)	0.2789(8)	0.3491(11)	0.6101(6)	0.4294(4)	1.0524(8)
O5	0.2347(10)	0.0593(6)	0.2672(11)	0.8879(7)	0.3127(6)	1.1473(9)
C1	0.1784(14)	0.3414(12)	0.0136(14)	0.6148(8)	0.1405(6)	0.9183(10)
C2	0.2863(16)	0.2345(24)	−0.0208(20)	0.7789(7)	0.0619(6)	0.9621(9)
C3	0.1751(11)	0.2199(9)	0.1085(12)	0.7319(7)	0.2204(5)	1.0462(9)
C4	0.1347(8)	0.2528(8)	0.3254(12)	0.6604(7)	0.3770(6)	1.0146(9)
C5	0.2429(11)	0.1162(8)	0.2741(11)	0.8338(8)	0.3029(7)	1.0726(10)
C6	0.4084(7)	0.2177(5)	0.4279(8)	0.7789(6)	0.2764(6)	0.7366(9)
C7	0.4048(7)	0.2329(5)	0.3116(8)	0.7713(6)	0.2029(5)	0.7427(8)
C8	0.3378(7)	0.3150(5)	0.3016(9)	0.6697(6)	0.2235(5)	0.7172(8)
C9	0.3448(8)	0.1943(7)	0.5567(10)	0.7708(9)	0.4019(7)	0.8132(11)
C10	0.3120(10)	0.1293(8)	0.5447(12)	0.7893(14)	0.4072(10)	0.7057(15)
C11	0.2728(11)	0.2694(9)	0.5971(14)	0.8423(16)	0.4134(11)	0.9093(20)
C12	0.4356(10)	0.1745(10)	0.6374(12)	0.6807(14)	0.4651(8)	0.8254(22)
C13	0.4298(10)	0.1096(7)	0.1922(11)	0.9100(6)	0.1328(6)	0.8845(9)
C14	0.3761(13)	0.0638(9)	0.1073(14)	0.9234(7)	0.0561(6)	0.8123(10)
C15	0.4929(11)	0.1191(9)	0.1371(13)	0.9603(7)	0.1714(8)	0.8542(11)
C16	0.4848(11)	0.0659(7)	0.2963(13)	0.9478(7)	0.1189(6)	1.0100(10)
C17	0.4424(7)	0.3699(5)	0.3349(9)	0.6600(6)	0.1642(5)	0.5335(7)
C18	0.4848(7)	0.4038(5)	0.4296(9)	0.6991(8)	0.0859(6)	0.5322(10)
C19	0.5658(8)	0.4059(6)	0.4363(10)	0.7331(9)	0.0411(6)	0.4387(12)
C20	0.6081(7)	0.3771(6)	0.3494(10)	0.7301(10)	0.0722(8)	0.3529(12)
C21	0.5646(8)	0.3439(7)	0.2491(11)	0.6947(10)	0.1493(8)	0.3536(11)
C22	0.4842(8)	0.3394(6)	0.2401(9)	0.6584(9)	0.1959(7)	0.4446(9)
C23	0.6974(10)	0.3783(9)	0.3573(15)	0.7683(14)	0.0232(10)	0.2549(14)
C24	0.1784(7)	0.3882(6)	0.3009(11)	0.5459(6)	0.3086(5)	0.8045(8)
C25	0.0937(9)	0.4105(9)	0.2256(13)	0.4985(7)	0.3540(6)	0.7178(9)
C26	0.0245(10)	0.4752(10)	0.2542(16)	0.4089(7)	0.4047(6)	0.7104(9)
C27	0.0353(8)	0.5197(8)	0.3597(13)	0.3658(6)	0.4087(6)	0.7933(10)
C28	0.1215(9)	0.4942(7)	0.4334(14)	0.4156(7)	0.3647(6)	0.8779(9)
C29	0.1912(7)	0.4299(7)	0.4053(11)	0.5040(7)	0.3161(6)	0.8886(8)
C30	−0.370(11)	0.5894(11)	0.3924(22)	0.2676(8)	0.4628(8)	0.7773(13)

TABLE II. Geometric Parameters (e.s.d.) of $Ru_2(CO)_5$(AIP {t-Bu, *p*-Tol}).

	Molecule A	Molecule B		Molecule A	Molecule B
Selected bond lengths in Å[a]					
The metal carbonyl part			The ligand part		
Ru(1)–Ru(2)	2.777(4)	2.780(3)	N(1)–C(6)	1.29(2)	1.25(1)
Ru(1)–C(1)	1.858(19)	1.868(16)	C(6)–C(7)	1.52(2)	1.52(2)
Ru(1)–C(2)	1.617(26)	1.857(11)	N(2)–C(7)	1.49(1)	1.50(1)
Ru(1)–C(3)	2.005(23)	1.988(10)	C(7)–C(8)	1.53(1)	1.54(1)
Ru(2)–C(3)	2.090(14)	2.051(14)	N(3)–C(8)	1.27(2)	1.27(1)
Ru(2)–C(4)	1.913(15)	1.914(10)	N(4)–C(8)	1.40(2)	1.40(1)

(Continued on facing page)

TABLE II. *(Continued)*

	Molecule A	Molecule B		Molecule A	Molecule B
Ru(2)–C(5)	1.852(18)	1.860(12)	N(1)–C(9)	1.50(2)	1.48(2)
C(1)–O(1)	1.15(3)	1.17(2)	N(2)–C(13)	1.52(1)	1.53(1)
C(2)–O(2)	1.40(3)	1.15(1)	N(3)–C(17)	1.41(2)	1.40(2)
C(3)–O(3)	1.17(2)	1.20(1)	N(4)–C(24)	1.45(1)	1.45(1)
C(4)–O(4)	1.13(2)	1.14(1)	C(20)–C(23)	1.50(2)	1.51(2)
C(5)–O(5)	1.17(2)	1.13(2)	C(27)–C(30)	1.47(2)	1.52(1)
			C–C(t-Bu):	1.53(1) (mean)	
			C–C(aryl):	1.39(1) (mean)	
The metal ligand part					
Ru(1)–N(2)	2.138(9)	2.145(11)			
Ru(1)–N(4)	2.187(10)	2.209(8)			
Ru(2)–N(1)	2.172(8)	2.229(12)			
Ru(2)–N(2)	2.141(13)	2.139(7)			
Ru(2)–N(4)	2.179(12)	2.199(8)			
Selected bond angles (°)					
The metal carbonyl part			Around Ru(2)		
Ru(1)–C(1)–O(1)	168.6(25)	177.2(10)			
Ru(1)–C(2)–O(2)	163.3(39)	179.7(9)	N(1)–Ru(2)–C(3)	164.6(7)	163.2(3)
Ru(1)–C(3)–O(3)	135.4(16)	134.2(10)	N(1)–Ru(2)–C(4)	101.9(5)	103.3(5)
Ru(2)–C(3)–O(3)	139.1(18)	138.8(9)	N(1)–Ru(2)–C(5)	96.5(5)	98.7(6)
Ru(2)–C(4)–O(4)	177.5(14)	178.5(13)	N(1)–Ru(2)–N(2)	80.1(4)	79.9(3)
Ru(2)–C(5)–O(5)	174.9(14)	179.0(14)	N(1)–Ru(2)–N(4)	86.3(4)	85.7(4)
			N(1)–Ru(2)–Ru(1)	118.9(3)	118.8(2)
Around Ru(1)			C(3)–Ru(2)–C(4)	91.2(6)	91.8(5)
C(1)–Ru(1)–C(2)	77.2(13)	83.7(5)	C(3)–Ru(2)–C(5)	92.2(7)	89.2(6)
C(1)–Ru(1)–C(3)	98.0(10)	98.6(5)	C(3)–Ru(2)–N(2)	85.4(6)	83.7(4)
C(1)–Ru(1)–N(2)	170.2(7)	170.5(4)	C(3)–Ru(2)–N(4)	84.2(6)	85.8(4)
C(1)–Ru(1)–N(4)	100.4(6)	99.6(4)	C(3)–Ru(2)–Ru(1)	46.0(6)	45.6(3)
C(1)–Ru(1)–Ru(2)	130.0(8)	128.0(3)	C(4)–Ru(2)–C(5)	87.0(7)	87.1(5)
C(2)–Ru(1)–C(3)	109.7(16)	97.6(4)	C(4)–Ru(2)–N(2)	167.7(6)	166.3(4)
C(2)–Ru(1)–N(2)	108.6(11)	104.6(5)	C(4)–Ru(2)–N(4)	96.0(6)	94.9(4)
C(2)–Ru(1)–N(4)	164.3(16)	173.8(4)	C(4)–Ru(2)–Ru(1)	121.0(5)	119.1(4)
C(2)–Ru(1)–Ru(2)	141.9(17)	130.7(4)	C(5)–Ru(2)–N(2)	104.9(6)	105.6(4)
C(3)–Ru(1)–N(2)	87.6(5)	85.0(5)	C(5)–Ru(2)–N(4)	175.3(5)	174.6(5)
C(3)–Ru(1)–N(4)	86.0(5)	87.1(4)	C(5)–Ru(2)–Ru(1)	124.7(5)	123.7(4)
C(3)–Ru(1)–Ru(2)	48.6(3)	47.5(4)	N(2)–Ru(2)–N(4)	71.9(4)	72.0(3)
N(2)–Ru(1)–N(4)	71.8(3)	71.7(3)	N(2)–Ru(2)–Ru(1)	49.5(2)	49.6(3)
N(2)–Ru(1)–Ru(2)	49.6(3)	49.4(2)	N(4)–Ru(2)–Ru(1)	50.6(3)	51.1(2)
N(4)–Ru(1)–Ru(2)	50.4(3)	50.7(2)			
The ligand part					
C(6)–N(1)–Ru(2)	108.8(7)	107.8(9)	Ru(2)–N(4)–C(8)	112.4(6)	112.1(7)
C(6)–N(1)–C(9)	119.4(9)	122.5(12)	Ru(2)–N(4)–C(24)	119.1(9)	120.0(5)
C(9)–N(1)–Ru(2)	131.8(9)	129.7(7)	C(7)–N(2)–C(13)	110.0(9)	111.3(8)
N(1)–C(6)–C(7)	119.4(9)	120.2(12)	C(8)–N(4)–C(24)	118.7(9)	118.5(7)
C(6)–C(7)–N(2)	109.7(11)	110.5(8)	C(7)–C(8)–N(4)	109.9(10)	109.4(7)
C(6)–C(7)–C(8)	103.7(8)	104.4(7)	C(7)–C(8)–N(3)	127.6(10)	125.3(9)
N(2)–C(7)–C(8)	104.9(7)	105.6(9)	N(4)–C(8)–N(3)	122.5(8)	125.3(9)
Ru(1)–N(2)–Ru(2)	80.9(4)	80.9(3)	C(8)–N(3)–C(17)	122.1(8)	120.0(8)
Ru(1)–N(4)–Ru(2)	79.0(3)	78.2(2)			
Ru(1)–N(2)–C(7)	107.0(6)	107.5(6)	C–C–C(t-Bu)	109.3(5) (mean)	
Ru(1)–N(2)–C(13)	125.4(7)	124.8(7)	C–C–N(t-Bu)	109.6(7) (mean)	
Ru(2)–N(2)–C(7)	100.7(7)	100.0(5)	C–C–C(aryl)	120.3(7) (mean)	
Ru(2)–N(2)–C(13)	126.6(10)	127.1(6)	C–C–N(aryl)	120.6(4) (mean)	
Ru(1)–N(4)–C(8)	92.3(7)	93.2(5)			
Ru(1)–N(4)–C(24)	127.3(7)	126.4(8)			

[a] Throughout this paper, standard deviations of mean values are calculated by $\sigma = \{\chi_i(\chi_i - \chi)^2/N(N-1)\}^{1/2}$.

Crystal Structure Determination of $Ru_2(CO)_5$(i-PrN=CHC(H)(N-i-Pr)C(S)$C_{12}H_8$) (Pentacarbonyl[1,4-diisopropyl-1,4-diaza-1-butene-3-{9-mercapto}-fluorenyl]-diruthenium: $C_{26}H_{24}N_2O_5RuS$)

Crystals of the title compound were orthorhombic, space group $P2_12_12_1$. The crystals were of poor quality, but several attempts to prepare better ones were unsuccessful and one crystal of 0.08 × 0.18 × 0.32 mm was selected. The unit cell had the dimensions: a =14.822(5), b = 16.951(28) and c = 25.413(16) Å; Z = 8, V = 6385.0 Å^3, d_c = 1.41 g cm^{-3}. A total of 6182 reflections with $\theta < 25°$ were measured on a NONIUS CAD4 diffractometer using graphite monochromated MoKα radiation. 1304 Reflections ($0 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 17$, $0 \leqslant l \leqslant 25$) had intensities above the $3\sigma(I)$ level and the remaining ones were treated as unobserved. No absorption correction was applied (μ = 10.22 cm^{-1}).

The positions of the four Ru-atoms in the asymmetric unit were derived from an E^2-Patterson synthesis. The remaining non-hydrogen atoms were obtained from subsequent ΔF-syntheses. Refinement proceeded by means of block-diagonal least-squares calculations. In view of the relatively small number of reflections (1304 for 72 non-hydrogen atoms), only Ru and S were refined anisotropically while the other atoms were treated isotropically. The refinement converged to R = 0.047, and this value did not improve when the enantiomorphic structure was refined. The anomalous scattering of Ru and S was taken into account and a weighting scheme of $w = 1/(67 + F_o + 0.0044F_o^2)$ was employed (R_w = 0.092). No extinction correction was applied. The computer programs used for plotting, the scattering factors and the dispersion correction were taken from the literature [11].

TABLE III. Atomic Coordinates (e.s.d.) of $Ru_2(CO)_5$(i-PrN=CHC(H)(N-i-Pr)C(S)$C_{12}H_8$.

Atoms	x (σ_x)	y (σ_y)	z (σ_z)	Atoms	x (σ_x)	y (σ_y)	z (σ_z)
Ru (1A)	0.0599(2)	0.4739(2)	0.6833(2)	C (9A)	0.415(2)	0.444(2)	0.6722(15)
Ru (1B)	0.5117(2)	0.3076(2)	−0.0487(1)	C (9B)	0.326(2)	0.159(2)	−0.1710(15)
Ru (2A)	0.1028(2)	0.4878(2)	0.7906(2)	C (10A)	0.371(3)	0.422(2)	0.632(2)
Ru (2B)	0.6536(2)	0.3256(2)	−0.1211(1)	C (10B)	0.360(3)	0.179(2)	−0.219(2)
S (A)	0.1984(7)	0.5336(6)	0.7140(5)	C (11A)	0.391(3)	0.394(2)	0.581(2)
S (B)	0.4860(6)	0.3354(6)	−0.1414(4)	C (11B)	0.323(2)	0.165(2)	−0.2683(14)
O (1A)	−0.074(2)	0.555(2)	0.7517(12)	C (12A)	0.330(3)	0.369(3)	0.542(2)
O (1B)	0.642(2)	0.425(2)	−0.0260(12)	C (12B)	0.363(3)	0.194(2)	−0.313(2)
O (2A)	0.014(2)	0.600(2)	0.6070(13)	C (13A)	0.236(3)	0.367(3)	0.558(2)
O (3B)	0.546(2)	0.253(2)	0.0592(11)	C (13B)	0.443(3)	0.244(2)	−0.309(2)
O (3A)	−0.099(3)	0.390(2)	0.644(2)	C (14A)	0.211(3)	0.394(3)	0.607(2)
O (2B)	0.395(2)	0.430(2)	−0.0003(14)	C (14B)	0.481(2)	0.257(2)	−0.2568(15)
O (4A)	−0.035(2)	0.424(2)	0.8641(13)	C (15A)	0.274(2)	0.418(2)	0.650(2)
O (4B)	0.838(2)	0.307(2)	−0.0727(11)	C (15B)	0.440(2)	0.224(2)	−0.2172(14)
O (5A)	0.101(2)	0.642(2)	0.8428(14)	C (16A)	0.071(3)	0.310(2)	0.7491(14)
O (5B)	0.706(2)	0.481(2)	−0.1626(13)	C (16B)	0.646(2)	0.161(2)	−0.0614(14)
N (1A)	0.116(2)	0.391(2)	0.7368(13)	C (17A)	0.102(3)	0.269(2)	0.800(2)
N (1B)	0.588(2)	0.220(2)	−0.0933(12)	C (17B)	0.713(3)	0.113(2)	−0.092(2)
N (2A)	0.223(2)	0.429(2)	0.8287(12)	C (18A)	0.078(3)	0.263(2)	0.697(2)
N (2B)	0.670(2)	0.251(2)	−0.1851(13)	C (18B)	0.581(3)	0.097(2)	−0.038(2)
C (1A)	0.222(2)	0.374(2)	0.7367(14)	C (19A)	0.260(3)	0.437(2)	0.880(2)
C (1B)	0.552(2)	0.182(2)	−0.1405(13)	C (19B)	0.734(3)	0.252(2)	−0.236(2)
C (2A)	0.255(2)	0.380(2)	0.7921(14)	C (20A)	0.211(4)	0.377(3)	0.908(2)
C (2B)	0.619(2)	0.188(2)	−0.1857(15)	C (20B)	0.727(4)	0.334(4)	−0.261(3)
C (3A)	0.270(2)	0.443(2)	0.702(2)	C (21A)	0.253(4)	0.519(3)	0.903(2)
C (3B)	0.465(2)	0.227(2)	−0.1603(15)	C (21B)	0.836(3)	0.251(3)	−0.205(2)
C (4A)	0.370(2)	0.465(2)	0.7188(13)	C (22A)	0.002(3)	0.518(2)	0.738(2)
C (4B)	0.379(2)	0.187(2)	−0.1314(14)	C (22B)	0.619(3)	0.377(3)	−0.059(2)
C (5A)	0.399(2)	0.498(2)	0.765(2)	C (23A)	0.022(3)	0.552(3)	0.639(2)
C (5B)	0.363(3)	0.179(2)	−0.082(2)	C (24B)	0.531(2)	0.227(2)	0.0089(14)
C (6A)	0.497(4)	0.515(3)	0.770(2)	C (24A)	−0.027(4)	0.421(3)	0.657(2)
C (6B)	0.287(3)	0.137(3)	−0.067(2)	C (23B)	0.440(3)	0.381(3)	−0.018(2)
C (7A)	0.543(3)	0.494(2)	0.7218(15)	C (25A)	0.027(3)	0.453(3)	0.838(2)
C (7B)	0.234(3)	0.103(2)	−0.104(2)	C (25B)	0.767(3)	0.313(2)	−0.092(2)
C (8A)	0.517(3)	0.465(3)	0.676(2)	C (26A)	0.104(4)	0.574(3)	0.825(2)
C (8B)	0.248(3)	0.117(2)	−0.153(2)	C (26B)	0.685(3)	0.416(3)	−0.145(2)

TABLE IV. Geometric Parameters (e.s.d.) of $Ru_2(CO)_5$(i-PrN=CHC(H)(N-i-Pr)C(S)$C_{12}H_8$).

	Molecule A	Molecule B		Molecule A	Molecule B
Selected bond lenghts					
The metal carbonyl part					
Ru(1)–Ru(2)	2.810(7)	2.811(6)	N(1)–C(1)	1.60(4)	1.46(5)
Ru(1)–C(22)	1.80(5)	2.00(5)	C(1)–C(2)	1.48(5)	1.54(6)
Ru(2)–C(22)	2.07(5)	1.87(5)	N(2)–C(2)	1.34(4)	1.31(5)
Ru–C(terminal)	1.74(4) (mean)		N(1)–C(16)	1.56(5)	1.55(5)
C(22)–O(1)	1.34(6)	1.22(6)	N(2)–C(19)	1.41(6)	1.61(6)
C–O(terminal)	1.22(3) (mean)		S–C(3)	1.89(4)	1.92(5)
			C(1)–C(3)	1.63(6)	1.58(6)
The metal ligand part			C(3)–C(4)	1.59(5)	1.62(6)
Ru(1)–S	2.42(1)	2.43(1)	C(3)–C(15)	1.39(7)	1.50(7)
Ru(1)–N(1)	2.13(3)	2.18(3)	C–C(i-Pr)	1.54(3) (mean)	
Ru(2)–S	2.53(1)	2.54(1)	C–C(aryl)	1.40(2) (mean)	
Ru(4)–N(1)	2.14(3)	2.16(3)			
Ru(2)–N(2)	2.07(5)	2.07(3)			
Selected bond angles (mean values)					
The metal carbonyl part		Around Ru(2)			
Ru(1)–C(22)–O(1)	133(11)	S–Ru(2)–C(22)	82(1)		
Ru(2)–C(22)–O(1)	135(11)	S–Ru(2)–C(25)	171(3)		
Ru–C–O(terminal)	173(5)	S–Ru(2)–C(26)	98(1)		
S–Ru(1)–C(22)	86(3)	S–Ru(2)–N(1)	72(1)		
S–Ru(1)–C(23)	100(1)	S–Ru(2)–N(2)	91(1)		
S–Ru(1)–C(24)	171(1)	C(22)–Ru(2)–C(25)	91(3)		
S–Ru(1)–N(1)	74(1)	C(22)–Ru(2)–C(26)	92(5)		
C(22)–Ru(1)–C(23)	94(3)	C(22)–Ru(2)–N(1)	85(4)		
C(22)–Ru(1)–C(24)	100(1)	C(22)–Ru(2)–N(2)	165(2)		
C(22)–Ru(1)–N(1)	87(1)	C(25)–Ru(2)–C(26)	88(2)		
C(23)–Ru(1)–C(24)	85(1)	C(25)–Ru(2)–N(1)	102(2)		
C(23)–Ru(1)–N(1)	174(1)	C(25)–Ru(2)–N(2)	96(2)		
C(24)–Ru(1)–N(1)	100(1)	C(26)–Ru(2)–N(1)	169(1)		
		C(26)–Ru(2)–N(2)	101(3)		
		N(1)–Ru(2)–N(2)	81(2)		
The ligand part					
Ru(1)–S–Ru(2)	69.0(2)	Ru(2)–N(2)–C(19)	133(1)		
Ru(1)–N(1)–Ru(2)	82(1)	N(1)–C(1)–C(2)	110(1)		
Ru(1)–S–C(3)	94.7(2)	N(1)–C(1)–C(3)	109(2)		
Ru(2)–S–C(3)	100(1)	N(2)–C(2)–C(1)	120(6)		
Ru(1)–N(1)–C(1)	121(1)	C(1)–N(1)–C(16)	108(3)		
Ru(1)–N(1)–C(16)	120(3)	C(2)–N(2)–C(19)	117(7)		
Ru(2)–N(1)–C(1)	104(1)	C(2)–C(1)–C(3)	107(2)		
Ru(2)–N(1)–C(16)	119(2)				
Ru(2)–N(2)–C(2)	110(6)	C–C–C(aryl)	120(2) (mean)		

The molecular geometry of $Ru_2(CO)_5$(i-PrN=CHC(H)(N-i-Pr)C(S)$C_{12}H_8$) (molecule A) with the numbering of the atoms is shown in Fig. 3. Atomic parameters, selected bond lengths and angles are given in Tables III and IV.

Analytical Data

All complexes gave satisfactory results for C, H and N microanalysis. The complexes showed characteristic ν(CO)-IR absorptions which are listed in Table V, together with the FD-mass data.

Results and Discussion

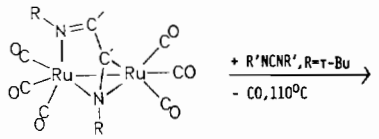
Formation of the Complexes

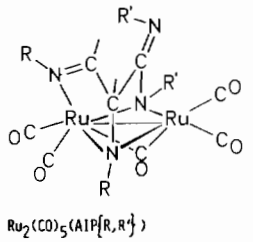
The C(t-Bu-DAB)–C(carbodiimide) coupled products are formed according to the reaction of eqn. (1):

TABLE V. IR- and FD-Mass Data.

Compound	M[a] (calc)	IR[b]: ν(CO) (in cm^{-1})
$Ru_2(CO)_5$(AIP{t-Bu, R'})		
R' = *p*-Tol	733(732.8)	2043(s), 2008(vs), 1977(vs), 1948(s), 1810(s)
R' = i-Pr	638(636.7)	2034(s), 2000(vs), 1967(vs), 1940(s), 1805(s)
R' = c-Hex	718(716.8)	2034(s), 1999(vs), 1965(vs), 1939(s), 1806(s)
$Ru_2(CO)_5$(RN=CHC(H)(NR)C(S)$C_{12}H_8$)		
R = i-Pr	680(678.7)	2043(s), 2009(vs), 1975(vs), 1953(s), 1790(m)
R = t-Bu	708(706.7)	2040(s), 2009(vs), 1972(vs), 1951(s), 1790(m)
R = c-Hex	759(758.8)	2039(s), 2007(vs), 1974(vs), 1951(s), 1788(m)

[a] The observed M values account for highest peak of the isotope pattern, the calculated values are based on ^{101}Ru. [b] In hexane.





(1)

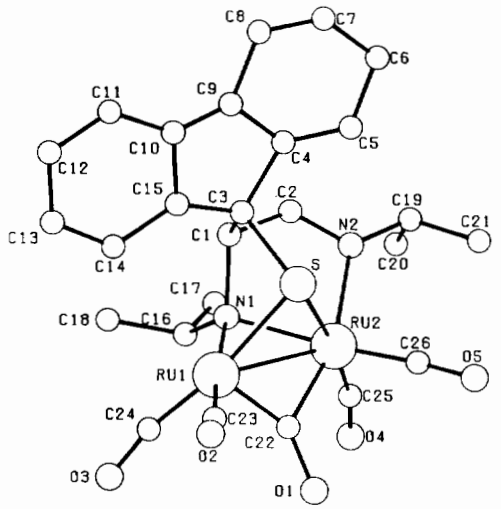
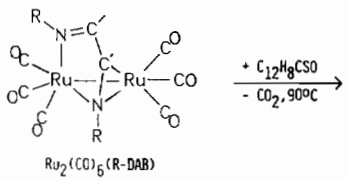
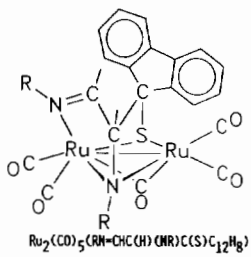


Fig. 3. The molecular geometry of $Ru_2(CO)_5$(i-PrN=CHC(H)-(N-i-Pr)C(S)$C_{12}H_8$).

The reaction route can be viewed as an insertion of one C=N double bond of the carbodiimide into the Ru–C(t-Bu-DAB) bond, thereby reducing one C=N bond of both ligands (reductive coupling). Although insertion reactions (*i.e.* M–X + Y → M–Y–X) are well documented for X = H and Y = olefin, alkyne or CO, other types involving other X and Y groupings are known [12]. Carbodiimides for example have been found to insert into M–C bonds (M = main group metal [12b], Nb, Ta [13]), into M–H bonds (M = Os, Ru) yielding formamidino complexes [14], or into M–N bonds (M = Ti, Zr) [15].

The reaction of $Ru_2(CO)_6$(R-DAB) with thiofluorenone-S-oxide ($C_{12}H_8CSO$) is shown schematically in eqn. (2).





(2)

Evolution of CO_2 was observed using IR-spectroscopy. During the reaction an imine- and a thioketone-function are reductively C–C coupled (or the reaction can be viewed as an insertion of a C=S-bond into a Ru–C(R-DAB)-bond). Evidently, the sulphine is deoxygenated by the metal carbonyl, with loss of CO_2. It has already been reported that sulphines are readily deoxygenated by metal carbonyls ($Fe(CO)_5$, $Mn_2(CO)_{10}$), yielding CO_2 and thioketone-organometallic species [16]. Sulphines thus bear some resemblance to trimethylamine-oxide, which often

reacts analogously with metal carbonyls with concomitant loss of CO_2 (see *e.g.* ref. [3]).

It is noteworthy that reaction of $Ru_2(CO)_6$(R-DAB) with another sulphine that is sterically more demanding than the flat $C_{12}H_8CSO$, *i.e.* (*p*-Tol-S)$_2$-CSO, does not yield analogous C–C coupled products. This may be due to steric constraints, but electronic effects cannot be ruled out* [17].

Before considering the reaction route in more detail, the molecular structures of these novel C–C bonded coupling products will be discussed.

Molecular Structure of $Ru_2(CO)_5$(AIP{t-Bu, p-Tol})

There are two independent molecules in the unit cell having only slightly different geometries. The molecular geometry of molecule B is shown in Fig. 2, together with the atomic numbering. Atomic coordinates and selected geometric parameters are given in Tables I and II, respectively.

The metal carbonyl part is a $(\mu\text{-CO})[Ru(CO)_2]_2$ unit with two terminal CO groups bonded to each Ru-atom. The bridging C(3)O(3) group can be considered as being a slightly asymmetrical bridge: Ru(1)–C(3) = 2.00; Ru(2)–C(3) = 2.07 Å (mean); Ru(1)–C(3)–O(3) = 134.8; Ru(2)–C(3)–O(3) = 139.0° (mean). The Ru(1)–Ru(2) bond length of 2.78 Å (mean) is rather long. In other diruthenium CO-bridged species, Ru–Ru single bond lengths between 2.70 and 2.75 Å are generally found [3, 6]. The exceptional bond lengths involving C(2) in molecule A (see Tables I and II) appear to be the result of error in positioning this atom since the non-bonding Ru(1)–O(2) distance is normal.

The t-Bu-N(1)=C(6)–C(7)–N(2)-t-Bu skeleton of the former t-Bu-DAB ligand is coupled to the *p*-Tol-N(3)=C(8)–N(4)-*p*-Tol skeleton of the former carbodiimide molecule via a single C–C bond: C(7)–C(8) = 1.53 Å (mean). Both N(1)=C(6) and N(3)=C(8) bonds are still imine bonds, each with double bond lengths of 1.27 Å (mean). This value may be compared with the N=C bond lengths of 1.258(3) Å in free c-Hex-DAB [18]. The intra-ligand bond angles around (N1), C(6) and N(3), being *ca.* 120°, are in accord with a sp^2-hybridization of these atoms while the slightly differing bond angles around C(8) are most probably due to the constraint in this part of the ligand resulting from coordination of N(4). The C(7)–N(2) bond, that in the starting complex $Ru_2(CO)_6$(t-Bu-DAB) had been η^2-coordinated to Ru(1), is clearly reduced to a single bond, as evidenced by the bond length of 1.50 (mean) Å and the bond angles around C(7) of 106.5° (mean). The somewhat shorter C(8)–N(4) bond length of 1.40 Å (mean) may be due to the shortening effect of the *p*-Tol-N(3)–C(8) moiety. The *p*-Tol- and t-Bu-groupings exhibit normal bond lengths and angles. It is also clear from the observed torsion angle of 35° (mean) around the central C(7)–C(6) bond that the character of the former α-diimine ligand has indeed changed markedly upon the C–C bond formation. In the free ligand or in symmetrically 4e- and 8e-bonded R-DAB complexes the diimine's skeleton is planar with corresponding torsion angles close to 0°, while in asymmetrically 6e-bonded R-DAB complexes the diimine's skeleton shows a maximum torsion angle of about 13° [19]. The torsion angle around the new N(2)C(7)–C(8)N(4) bond in the present compound is 33° (mean).

The AIP ligand is bonded to the two Ru-atoms via three of the four N-atoms, with N(2) and N(4) in symmetrically bridging positions. All bonding Ru–N distances are normal. Only N(3) is clearly positioned at a non-bonding distance (>3 Å) from both Ru-atoms.

Assuming a single, 2e–2c Ru–Ru bond, both metals obey the 18e-rule. In an analogous C–C coupled product, *i.e.* $Ru_2(CO)_5$(R-IAE) (see Fig. 1), the fourth N-atom is also coordinated to Ru. As a consequence no Ru–Ru bond is thought to be present in the latter complex [4].

The Molecular Structure of $Ru_2(CO)_5$(i-PrN=CHC(H)(N-i-Pr)C(S)$C_{12}H_8$)

Again, there are two independent molecules in the unit cell, one of which (A) is shown in Fig. 3, together with the atomic numbering. Atomic coordinates and selected bond lengths and angles are given in Tables III and IV.

Due to the low number of reflections, the e.s.d. s of the geometric parameters are relatively high, but nevertheless the overall geometry exhibits normal features.

Each Ru-atom is coordinated by two terminal carbonyl groups with normal Ru–C bond lengths of 1.75 Å (mean) and bond angles of 173° (mean). One carbonyl C(22)O(1) is bridging the Ru–Ru single bond, that has a bond length of 2.811 Å (mean).

The i-Pr-DAB ligand (i-Pr-N(1)–C(1)–C(2)=N(2)-i-Pr) is coupled to the 9-mercapto-fluorenyl moiety (S–C(3)$C_{12}H_8$) via a single C(1)–C(3) bond of 1.61 Å (mean). Consequently, one imine bond of the former α-diimine ligand is clearly reduced to a single bond (N(1)–C(1) = 1.53 Å (mean)) while the bond length of N(2)=C(2) of 1.32 Å (mean) is indicative of a double bond. Both C(1)–C(2)- and S–C(3) bond lengths of 1.51(3) and 1.91(2) (mean), respectively, are as expected for single bonds [20]. The bond lengths and angles in the aryl rings and the i-Pr groupings are within the normal ranges.

*The conclusion that electronic influences may be important is based on the fact that deoxygenation of sulphines is also observed in reactions of some R_2SnX_2-species with both $C_{12}H_8CSO$ and amino-sulphines, *i.e.* sulphines in which conjugation is present between the π-system of the sulphine group and the π system of the substituents.

The ligand is coordinated to the two Ru-atoms via N(2) (to Ru(2) only) and via N(1) and S in bridging positions. Interestingly, S is asymmetrically bridging the Ru–Ru bond with significantly different bond lengths: Ru(1)–S = 2.43(1) Å (mean), Ru(2)–S = 1.54(1) Å (mean), with the latter value being rather large for a Ru–S single bond [21].

Comparison of C–C Coupled Products

Until now, there are only four examples known of C(R-DAB)–C(L) coupled species and all of them have been obtained from the reaction of $Ru_2(CO)_6$(R-DAB) with L (L = R-DAB [4], crystal structure of analogous compound, see ref. [22]; L = phenylacetylene [5a]; L = $C_{12}H_8CS$, *p*-Tol-carbodiimide [this article]). Interestingly, all these compounds exhibit the same $[Ru(CO)_2)]_2(\mu$-CO) metal carbonyl unit that is doubly bridged by a N–C–C–X moiety (see Fig. 4).

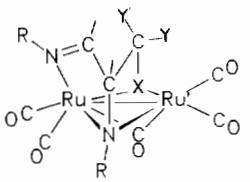


Fig. 4. The schematic structure of the C–C coupled products; L = R-DAB, X = NR, Y = C(H)NR, Y′ = H; L = Ph-C ≡ CH, X = Ph-C, YY′ = H; L = $C_{12}H_8CSO$, X = S, YY′ = $C_{12}H_8$; L = *p*-Tol-carbodiimide, X = N-*p*-Tol, YY′ = N-*p*-Tol.

The Y-groupings (see Fig. 4) may (L = R-DAB) or may not be coordinated to the Ru′-atom. In all complexes the imine bond of the α-diimine that has been η^2-bonded to Ru′, is reductively coupled to an unsaturated C=X function of another ligand. Another, analogous description of these structures is to view them as insertion products, *i.e.* the C=X bond has inserted into the Ru(2)–C(R-DAB) bond. Interestingly, until now this type of C–C bond formation between R-DAB and the pseudo alkene C=X has only been accomplished when both participant C-atoms bear at least one H-atom [4, 5a, 22]. The present species represent the first examples in which such H-atom on the incoming C=X function is absent, so that a still larger variety of C–C coupling reactions may be anticipated.

IR-ν(CO) Region

The present complexes have the general formula $Ru_2(CO)_5$(R-DAB-L), in which L is an organic fragment coupled to the R-DAB moiety, via a C–C bond. They all show characteristic absorption patterns in the ν(CO)-region (see Table V). There are four strong bands present between 2043 and 1939 cm^{-1} due to the four terminal carbonyls. The one medium band at *ca.* 1808 cm^{-1} (L = carbodiimide) or 1790 cm^{-1} (L = 9-mercapto-fluorenyl) is assigned to the stretching frequency of the bridging carbonyl. The spectra are very similar to those of other $Ru_2(CO)_5$-(R-DAB-L) coupled products, all of which contain the same $[Ru(CO)_2]_2(\mu$-CO) unit (*vide supra*) [3–5a].

FD-Mass Spectroscopy

FD-Mass spectroscopy (see Table V) has been extremely valuable for the identification and characterization of the new complexes. A big advantage of this technique is that generally only molecular ions are observed [9]. As a result, the stoichiometry of the present new compounds was immediately evident from the FD-mass results. In particular the FD-mass data revealed that in the reaction of $Ru_2(CO)_6$(R-DAB) with the sulphine $C_{12}H_8C{=}S{=}O$ the sulphine's oxygen was not incorporated in the product. From this, evolution of CO_2 during this reaction was suspected and subsequently detected by IR-spectroscopy.

^{1}H NMR Spectroscopy

The ^{1}H NMR data of the new complexes are listed in Table VI and are in accord with a molecular geometry in solution equivalent to that found in the solid state.

Both complex types contain a chiral N- and a chiral C-centre in the central N–C–C–X skeleton (see Fig. 4). However, the geometry is such that for both types only two isomers, that are enantiomeric, can be formed. Accordingly, the ^{1}H NMR spectra only show one resonance pattern.

The C–C coupling reaction between R-DAB and L (L = carbodiimide, 9-mercapto-fluorenyl) has made the former R-DAB ligand asymmetric. Consequently, the two R-groupings have different chemical shifts and the two central C(H) hydrogen atoms give rise to an AX-pattern. One H-atom resonates near 8 ppm, which is normal for an imine proton. The chemical shift of the other proton (*ca.* 5 ppm for L = carbodiimide; *ca.* 4 ppm for L = 9-mercapto-fluorenyl), indicates that the C=N double bond has been reduced to a single one. In analogous $Ru_2(CO)_5$(R-DAB-L) coupled products (L = R-DAB, acetylenes), similar chemical shift patterns are observed [3, 4].

The signals of the aryl protons of the fluorenyl part and the two non-equivalent R-groupings of the carbodiimide fragment have the expected resonance positions.

Interestingly, in the 250 MHz spectrum recorded at −50 °C, the high field singlet due to the t-Bu-grouping of the C–C coupled side of the ligand in $Ru_2(CO)_5$(t-BuN=CHC(H)(Nt-Bu)C(S)$C_{12}H_8$), is split into three singlets each having an integral of three

TABLE VI. ^{1}H NMR Data.

Compound	Chemical shifts[a] (multiplicity, J, number of H)			
$Ru_2(CO)_5$(AIP {t-Bu, R})	t-Bu	R-group	amine H	imine H
R = *p*-Tol[b,c]	0.89(s, 9H) 0.86(s, 9H)	7.70(d, 8Hz, 2H); 6.54(d, 8Hz, 2H) 6.89(d, 8Hz, 2H); 6.95(d, 8Hz, 2H) 2.15(s, 3H); 2.03(s, 3H)	5.13(d, 2Hz, 1H)	7.74(d, 2Hz, 1H)
R = i-Pr	1.34(s, 9H) 1.24(s, 9H)	4.10(sept, 6Hz, 1H); 3.64(sept, 6Hz, 1H) 1.43(d, 6Hz, 3H)/1.18(d, 6Hz, 3H) 1.08(d, 6Hz, 3H)/1.03(d, 6Hz, 3H)	5.35(d, 2Hz, 1H)	8.27(d, 2Hz, 1H)
R = c-Hex[c]	0.81(s, 9H) 0.70(s, 9H)	3.5(m, 1H); 3.0(m, 1H) 2–1(m, 2OH)	4.85(d, 2Hz, 1H)	7.50(d, 2Hz, 1H)
$Ru_2(CO)_5(RN{=}CHC(H){-}(NR)C(S)C_{12}H_8)$	fluorenyl	R-group	amine H	imine H
R = i-Pr	7.65(d, 6Hz, 1H) 7.64(d, 6Hz, 1H) 7.4–7.1(m, 5H) 6.83(d, 8Hz, 1H)	4.04(sept, 6Hz, 1H); 3.46(sept, 6Hz, 1H) 1.63(d, 6Hz, 3H)/1.43(d, 6Hz, 3H) 1.36(d, 6Hz, 3H)/0.91(d, 6Hz, 3H)	4.12(d, 2Hz, 1H)	7.60(d, 2Hz, 1H)
R = t-Bu	7.66(d, 6Hz, 1H) 7.62(d, 6Hz, 1H) 7.4–6.9(m, 6H)	1.51(s, 9H); 1.19(s, 9H)[e]	4.21(d, 2Hz, 1H)	7.59(d, 2Hz, 1H)
R = c-Hex	7.65(d, 6Hz, 1H) 7.63(d, 6Hz, 1H) 7.4–7.1(m, 5H) 6.83(d, 8Hz, 1H)	3.61(m, 1H); 2.86(m, 1H) 2.3–0.8(m, 2OH)	4.11(d, 2Hz, 1H)	7.54(d, 2Hz, 1H)

[a] The values are in ppm, relative to TMS, and have been obtained in $CDCl_3$ solution; d = doublet, s = singlet, m = multiplet, sept = septet; vertical bars separate diastereotopic pair; J is in Hz. [b] In solution *ca.* 0.4 equivalent of diethyl ether was also present. [c] In toluene-d_8 solution. [e] At −50 °C (250 MHz), this peak splits into three singlets with an integral of 3H each: 1.50, 1.18 and 0.73 ppm. Coalescence temperature: 20 °C (250 MHz).

protons. Other parts of the spectrum are unaffected. Evidently, this t-Bu grouping experiences a restricted rotation around the N-t-Bu bond, most likely due to steric interaction with the C(14)–H(14) part of the fluorenyl group (compare molecular geometry in Fig. 3). The chemical shift difference and the coalescence temperature (20 °C) suggests a ΔG^* value of *ca.* 14 kcal/mol.

Reaction Route

The reaction route leading to the C–C coupled products is presumably rather intricate. Reaction of $Ru_2(CO)_6$(R-DAB) with R-DAB itself, yielding the C–C coupled product $Ru_2(CO)_5$(R-IAE), occurs via a $Ru_2(CO)_5$(R-DAB) intermediate (see Fig. 1). So after prior CO-elimination the C–C coupling reaction takes place. Such a sequence is not likely in the case of the present reactions. This is because $Ru_2(CO)_5$(t-Bu-DAB), prepared *in situ*, reacts with carbodiimides to give only minor yields of $Ru_2(CO)_5$(AIP{t-Bu, R'}) (<10%), while extensive decomposition and formation of $Ru_2(CO)_5$(t-Bu-IAE) also occur. Similarly, whereas $Ru_2(CO)_6$(R-DAB) reacts with $C_{12}H_8CSO$ with loss of CO_2, the reaction of $Ru_2(CO)_5$(R-DAB) with the sulphine only gives decomposition products* [22]. These observations seem to point to a direct reaction between the hexacarbonyl Ru-species and the hetero-allene species (carbodiimide or sulphine) rather than to a reaction of these latter species with a $Ru_2(CO)_5$(R-DAB) intermediate. In the resulting products a C=X (X = N, S) bond is inserted into the Ru–C(R-DAB) bond of the η^2-bonded part of the R-DAB molecule. Such an insertion reaction, as is often found, may take place via a concerted mechanism§ [23–25]. Concomitant or subsequent loss of CO (carbodiimide reaction) or loss of CO_2 (sulphine reaction) occurs and a final rearrangement yields the products.

The fact that in the reaction of $Ru_2(CO)_6$(t-Bu-DAB) with R'NCNR' (R' = c-Hex, i-Pr) substantial amounts of $Ru_2(CO)_5$(t-Bu-IAE) are also formed (as evidenced by IR- and FD-mass-spectroscopy) may indicate that during the reaction free t-Bu-DAB is present as a reaction partner. It is known that $Ru_2(CO)_6$(t-Bu-DAB) reacts with t-Bu-DAB to yield $Ru_2(CO)_5$(t-Bu-IAE) almost quantitatively [4]. It is important to note that we found that refluxing $Ru_2(CO)_6$(t-Bu-DAB) on its own does not yield $Ru_2(CO)_5$(t-Bu-IAE). Therefore it seems likely that the free t-Bu-DAB, if present, originates from a substitution reaction of the starting complex with carbodiimide§§.

Accordingly, two concurrent reactions may play a role in the carbodiimide reaction. The first is an insertion reaction, yielding the C–C coupled product, which is relatively fast for R' = *p*-Tol, but slow for R' = i-Pr, c-Hex. The second, concurrent reaction involves a substitution of t-Bu-DAB by the carbodiimide and subsequent desintegration of the resulting complex. This reaction is slow for R' = *p*-Tol and relatively fast for R' = i-Pr, c-Hex. The free-t-Bu-DAB obtained, reacts further with $Ru_2(CO)_6$(t-Bu-DAB) to yield $Ru_2(CO)_5$(t-Bu-IAE) as a byproduct.

C–C vs. C–X Bond Formation

In the reactions of the early transition-metals with CO_2 like molecules, Floriani *et al.* studied reductive C–C coupling [26, 27], explained by a radical mechanism which is often a feature of reactions promoted by early-transition metals. They also noted that group VIII metals in low oxidation state, in reaction with C=X functional groups, usually yield asymmetric (*i.e.* C–X) coupled products [27]. The observed C–C coupling in reactions of $Ru_2(CO)_6$(R-DAB) with sulphines, carbodiimides [this study], α-diimines [3, 4], and acetylenes [5], therefore seems rather surprising. However our results may be explained by the polarity of the η^2-C=N coordinated imine bond of R-DAB.

In free R-DAB the imine-C-atom is (slightly) positively polarized whereas the N-atom is negatively so. However, η^2-C=N coordination tends to invert this original polarization: because the filled π-orbital, to which N contributes most, loses electron density to a metal–imine σ-bond, and because electron back-donation from the metal into the imine's π*-orbital, to which C contributes most, results in a build-up of electron density on the imine C-atom.

The C–C bond formation can then be made plausible because the C-atom in the carbodiimide ligand is positively polarized. In the case of the sulphine reaction, attack of the negatively polarized O-atom ($C=S=O \leftrightarrow C=S^+-O^-$) [28] on a carbonyl C-atom, yields CO_2 together with a thioketone function which is also positively polarized on the C-atom.

Conclusions

The C–C bond formation between the η^2-C=N coordinated imine moiety in $Ru_2(CO)_6$(R-DAB) and substrates L, is not restricted to L = R-DAB and alkynes [5, 6]. It has now been shown that sulphines,

*It is interesting to note that reaction of $Ru_2(CO)_5$(R-DAB) with the thioketone $(p\text{-Tol})_2C=S$ does not lead to C(thioketone)–C(R-DAB) coupled products.

§ After various other mechanistic proposals, the disproportionation reaction of $Fe(CO)_5$ with carbodiimides, R'NCNR', yielding $Fe_2(CO)_6(C-(NR')_2=NR')$, is now also believed to proceed via a concerted mechanism.

§§ Often when the reaction of $Ru_2(CO)_n$(R-DAB) (n = 5, 6) with an unsaturated species L (*e.g.* L = t-BuN=S=Nt-Bu, acetonitrile, *p*-Tol N=N-*p*-Tol, $(p\text{-Tol-S})_2C=S=O$, 4-aza-1-oxo-1,3-butadienes) does not yield insertion product, *i.e.* $Ru_2(CO)_5$(R-DAB-L), only $Ru_2(CO)_5$(R-IAE) is obtained in yields ranging from 10–60%.

with loss of an oxygen atom as CO_2, and carbodiimides may react analogously. Furthermore, for the first time C–C bond formation has occurred between an imine C(H)=N fragment and a C=X fragment that does not bear a H-atom on the coupled C-atom. Further investigations on possible C–C bond formation reactions and of the precise mechanisms involved are required.

Acknowledgements

We thank Mr. D. Heijdenrijk and Dr. J. de Boer for collecting the X-ray data, Mr. R. Fokkens for recording the mass spectra and Mr. J. M. Ernsting for recording the ^{1}H NMR spectra. Mr. R. Jans is thanked for his cooperation with the syntheses of the sulphines. We thank the Netherland Foundation for Chemical Research (S.O.N.) and the Netherland Organization for Pure Research (Z.W.O.) for their financial support.

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