Chemistry Derived from Ruthenium Atoms. 1.[1] Dimerization of Coordinated 2,3-Dimethylbutadiene Ligands in M(CO)(diene)$_2$ Complexes (M = Ru, Fe). Crystal Structure of Dicarbonyl[(1–3-η:6–8-η)-2,3,6,7-tetramethyloctadienediyl]ruthenium

David N. Cox and Raymond Roulet*

Institut de Chimie Minérale et Analytique de l'Université, CH-1005 Lausanne, Switzerland

Gervais Chapuis

Institut de Cristallographie de l'Université, Bâtiment des Sciences Physiques, CH-1015 Lausanne, Switzerland

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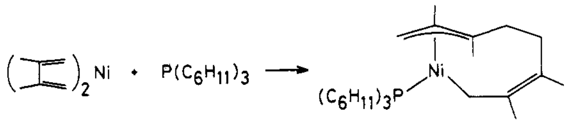
$Ru(CO)(\eta^4\text{-}C_6H_{10})_2$ (1) has been synthesized by cocondensation of 2,3-dimethylbutadiene and ruthenium atoms generated from an electron beam furnace, followed by addition of CO (1 atm) at 77 K. Unprecedented diene coupling reactions occurred on heating 1 or the related $Fe(CO)(\eta^4\text{-}C_6H_{10})_2$ (3) in THF under CO (1 atm) giving the bis(allyl) complexes $M(CO)_2(\eta^3{:}\eta^3\text{-}C_{12}H_{20})$ (M = Ru, 2; M = Fe, 4). Upon sublimation 2 crystallized in space group $P\bar{1}$ with $a = 7.330$ (2) Å, $b = 9.356$ (1) Å, $c = 11.008$ (3) Å, $\alpha = 87.01$ (2)°, $\beta = 82.96$ (2)°, $\gamma = 71.10$ (2)°, and $Z = 2$. The structure was refined to $R = 1.8\%$ for 1843 unique reflections with $2\theta = 3.5$–50.0° (Mo Kα radiation). The molecule has noncrystallographically imposed C_2 symmetry with the configuration of the bis(allyl) ligand retaining the cisoid conformation of the diene remnants.

Introduction

Zerovalent nickel compounds have been extensively studied as catalysts for the coupling of 1,3-dienes.[2,3] In addition, metal evaporation experiments have indicated that the majority of transition elements may also be capable of diene oligomerization.[4] Despite the wide range of active systems, the stoichiometric diene coupling reaction shown in eq 1 was previous to this work virtually unique. It represented the only example of a direct diene coupling reaction where the M(diene)$_2$-type precursor and the organometallic species bearing the coupling ligand had both been isolated.[5]



(1)

The activity of certain iron or ruthenium reagents in the oxidative coupling of dienes to produce a chelating bis(allyl) moiety has been established. Hence, $Fe(CO)_2(\eta^3{:}\eta^3\text{-}C_{12}H_{16})$ may be obtained from $Fe_3(CO)_{12}$ and 1,2-dimethylidenecyclobutane,[6] the unrelated $Ru(CO)_2(\eta^3{:}\eta^3\text{-}C_{12}H_{16})$ from $Ru(CO)_3(\eta^4\text{-}$1,3-cyclohexadiene) and cyclohexadiene,[7] and $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]_2$ from alcoholic solutions of $RuCl_3$ and isoprene.[8,9] In these systems, however, the coupling reaction was effected by diene addition and M(diene)$_2$-type precursors were not observed.

The wide variety of stable FeL(diene)$_2$ complexes that have been synthesized[10–12] could provide a source of potential M(diene)$_2$-type precursors for observing similar stoichiometric diene coupling reactions. Indeed, considering the known $\eta^2{:}\eta^2$ and $\eta^4{:}\eta^2$ oxidative cyclizations of olefin ligands around $Fe(CO)_3$ and $Fe(CO)_2$ centers,[13,14] a related $\eta^4{:}\eta^4$ diene coupling around an Fe(CO) center would seem plausible. This hypothetical reaction is generalized in eq 2. Perhaps surprisingly, no examples of such a ligand-induced transformation have previously been reported.[15]

(2)

M = Fe, Ru, Os L = 2-electron ligand

In view of the recent availability of Ru(CO)(diene)$_2$ complexes,[1] we decided to investigate the behavior of these five-coordinate species in the presence of additional ligand. The ease of reaction prompted us to examine an analogous iron complex, and we now report the first examples of ligand-induced diene coupling reactions (eq 2) in iron and ruthenium chemistry.

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(15) The small catalytic activity of $Fe(CO)(C_4H_6)_2$ in diene oligomerization or its decomposition liberating 1,5-cyclooctadiene in high yield perhaps involves such a step (Carbonaro, A.; Greco, A. *J. Organomet. Chem.* **1970**, *25*, 477).

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Results and Discussion

The only available general route to Ru(CO)(diene)$_2$ complexes is metal atom evaporation. Minniti and Timms[16] first reported the synthesis of Ru(CO)(η^4-butadiene)$_2$ although the small scale of their evaporation (resistance heated filament) hindered adequate characterization. In a preliminary communication,[1] we have since outlined related preparations of other Ru(CO)(diene)$_2$ complexes from Ru atom/diene condensates. The use of a positive hearth electron beam furnace to evaporate ruthenium atoms on a gram scale has allowed product isolation in synthetically viable quantities. Full details of the preparation and characterization of the 2,3-dimethylbutadiene derivative Ru(CO)(η^4-C_6H_{10})$_2$ (1) are given in the Experimental Section.

Carbonylation of Ru(CO)(η^4-C_6H_{10})$_2$ (1). Solutions of 1 in THF are readily carbonylated under mild conditions. The reaction is complete after 90-min reflux under CO (1 atm). This is evidenced by the IR spectra which indicate the total disappearance of 1 (ν(CO) = 1993 cm^{-1}) and the formation of a new species with ν(CO) stretches at 1947 and 2010 cm^{-1} (pentane solution). Vacuum sublimation (50 °C (10^{-4} mbar)) of the crude product resulted in the isolation of Ru(CO)$_2$ (η^3:η^3-$C_{12}H_{20}$) (2) as an air-stable pale yellow microcrystalline powder (40%). No trace of Ru(CO)$_3$(η^4-2,3-dimethylbutadiene) or any other ruthenium–carbonyl species was detected in the crude product.

Carbonylation of Fe(CO)(η^4-C_6H_{10})$_2$ (3). The carbonylation of THF solutions of 3 proceeds more slowly than that of 1. Reflux for 21 h under CO (1 atm) is required to effect the disappearance of 3 (ν(CO) 1971 cm^{-1}).[10] The IR spectra of the crude product indicated the formation of a mixture of carbonyl species which were separated by chromatography into two major components. Fe(CO)$_3$(η^4-2,3-dimethylbutadiene) was subsequently identified as the major product of the carbonylation (53%). The second component exhibited two ν(CO) stretches in the IR at 1930 and 1987 cm^{-1} (pentane solution). It was further purified by sublimation (20 °C (10^{-4} mbar)) and obtained as a moderately air-stable orange-red oil. It was characterized as Fe(CO)$_2$(η^3:η^3-$C_{12}H_{20}$) (4; 19%). Both 2 and 4 are inert to further carbonylation (prolonged reflux under 100 atm of CO).

NMR Data for 2 and 4. The NMR spectra of 2 and 4 are consistent with their formulation as chelating bis(allyl) species (2,3,6,7-tetramethyl substituted) of the type shown in eq 2. The ^{1}H NMR data for 2 and 4 show a direct correspondence of all the individual resonances to within 0.2 ppm. A similar quantitative correspondence ($\Delta\delta \leqslant 0.2$ ppm) is found in the two ^{13}C NMR spectra, with the exception of the resonances from the carbon atoms which are directly metal bonded. The allylic carbon atoms show a relative shift of ca. ±6 ppm between 2 and 4 and the single CO resonance shifts from 203.3 (2) to 217.5 ppm (4). Such close similarities suggest that 2 and 4 share a common molecular geometry.

The spectra are all temperature independent (−80 to +80 °C; toluene-d_8), and the two halves of the chelating bis(allyl) ligand are evidently chemically equivalent. An element of molecular symmetry, either a C_2 axis or a mirror plane, must account for this. In order to assign unambiguously the configuration of the organic ligand in these complexes, the molecular structure of 2 was determined by X-ray diffraction.

Molecular Structure of Ru(CO)$_2$(η^3:η^3-$C_{12}H_{20}$) (2). The molecular structure of 2, complete with the heavy-atom numbering system, is illustrated in Figure 1. The H atoms have been omitted for clarity but are numbered

Table I. Experimental Data for the X-ray Diffraction Study of 2

(A) Crystal Data

cryst system triclinic
a = 7.330 (2) Å
b = 9.356 (1) Å
c = 11.008 (3) Å
α = 87.01 (2)°
β = 82.96 (2)°
γ = 71.10 (2)°

space group: $P\bar{1}$
V = 708.8 (4) Å^3
Z = 2
mol wt = 321.38 amu
ρ(measd) = 1.49 g cm^{-3}
ρ(calcd) = 1.51 g cm^{-3}
μ(Mo Kα) = 10.73 cm^{-1}

(B) Data Collection

radiation: Mo K$\bar{\alpha}$, Nb filtered (λ = 0.71069 Å)
min and max transmission: 0.843, 0.869
2θ limits: 3.5–50.0°
scan width: [2θ(Kα_2) + 1.0] − [2θ(Kα_1) − 1.0]°
scan speed: variable (2–10° min^{-1})
scan type: θ(crystal)–2θ(counter)
bkgd from: scan profile interpretation[33]
reflctns measd: $\pm h, \pm k, \pm l$
reflctns collected: 3825 total, 1964 unique data, 1754 with $I > 3\sigma(I)$
std reflctns: 3 measured after each 97 reflctns (1,2,3; −2,1,2; 2,0,−4), no observed decay

Table II. Atom Coordinates and Equivalent Temperature Factors for 2[a]

atom	x	y	z	U_{eq} or U, Å^2
Ru	−0.043982 (3)	0.73528 (3)	0.72543 (2)	0.04340 (8)
C(1)	0.2056 (5)	0.6961 (5)	0.5796 (3)	0.068 (1)
C(2)	0.2529 (4)	0.5793 (3)	0.6660 (3)	0.055 (1)
C(3)	0.2547 (4)	0.6155 (3)	0.7885 (3)	0.053 (1)
C(4)	0.3360 (5)	0.7389 (4)	0.8155 (4)	0.071 (1)
C(5)	0.1816 (5)	0.8706 (4)	0.8791 (4)	0.076 (1)
C(6)	0.0159 (4)	0.9397 (3)	0.8021 (3)	0.063 (1)
C(7)	−0.1726 (4)	0.9364 (3)	0.8454 (3)	0.057 (1)
C(8)	−0.1898 (5)	0.8079 (4)	0.9097 (3)	0.058 (1)
C(9)	0.2814 (7)	0.4211 (5)	0.6247 (5)	0.083 (2)
C(10)	0.2789 (7)	0.4945 (5)	0.8876 (4)	0.080 (2)
C(11)	0.0444 (9)	1.0664 (5)	0.7208 (6)	0.107 (2)
C(12)	−0.3532 (6)	1.0609 (5)	0.8160 (5)	0.087 (2)
C(13)	−0.1322 (4)	0.5685 (4)	0.7309 (3)	0.061 (1)
C(14)	−0.2259 (5)	0.8336 (4)	0.6180 (3)	0.068 (1)
O(1)	−0.1964 (4)	0.4713 (3)	0.7414 (3)	0.102 (1)
O(2)	−0.3316 (4)	0.8879 (4)	0.5472 (3)	0.109 (1)
H(1)	0.244 (4)	0.782 (3)	0.588 (2)	0.055 (9)
H(2)	0.187 (4)	0.674 (3)	0.500 (3)	0.07 (1)
H(3)	0.388 (4)	0.773 (3)	0.737 (3)	0.064 (9)
H(4)	0.441 (5)	0.693 (4)	0.868 (3)	0.08 (1)
H(5)	0.236 (5)	0.953 (4)	0.898 (3)	0.09 (1)
H(6)	0.136 (4)	0.840 (3)	0.957 (3)	0.07 (1)
H(7)	−0.101 (4)	0.754 (3)	0.962 (2)	0.049 (8)
H(8)	−0.313 (4)	0.806 (3)	0.935 (2)	0.063 (9)
H(9)	0.253 (5)	0.364 (4)	0.690 (3)	0.08 (1)
H(10)	0.428 (6)	0.377 (5)	0.599 (4)	0.13 (1)
H(11)	0.220 (7)	0.425 (5)	0.548 (4)	0.16 (2)
H(12)	0.240 (5)	0.544 (4)	0.967 (3)	0.10 (1)
H(13)	0.227 (6)	0.414 (5)	0.875 (4)	0.13 (2)
H(14)	0.414 (5)	0.435 (4)	0.888 (3)	0.11 (1)
H(15)	0.181 (6)	1.035 (5)	0.673 (4)	0.13 (2)
H(16)	0.014 (6)	1.156 (5)	0.761 (4)	0.12 (2)
H(17)	−0.045 (6)	1.096 (5)	0.658 (4)	0.12 (2)
H(18)	−0.375 (5)	1.138 (5)	0.877 (4)	0.12 (1)
H(19)	−0.342 (6)	1.113 (5)	0.729 (4)	0.13 (2)
H(20)	−0.465 (6)	1.029 (4)	0.825 (4)	0.11 (2)

[a] $U_{eq} = [{}^1/_3(U_{11} + U_{22} + U_{33})]$.

Table III. Interatomic Distances (Å) and Esd's for 2

Ru–C(1)	2.227 (3)	C(1)–C(2)	1.394 (5)
Ru–C(2)	2.232 (2)	C(2)–C(3)	1.410 (4)
Ru–C(3)	2.287 (3)	C(2)–C(9)	1.512 (6)
Ru–C(6)	2.316 (3)	C(3)–C(4)	1.516 (5)
Ru–C(7)	2.231 (3)	C(3)–C(10)	1.514 (5)
Ru–C(8)	2.205 (3)	C(4)–C(5)	1.511 (5)
Ru–C(13)	1.869 (4)	C(5)–C(6)	1.516 (5)
Ru–C(14)	1.872 (3)	C(6)–C(7)	1.415 (4)
C(13)–O(1)	1.146 (5)	C(6)–C(11)	1.501 (7)
C(14)–O(2)	1.147 (4)	C(7)–C(8)	1.396 (5)
		C(7)–C(12)	1.510 (5)

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[16] Minniti, D.; Timms, P. L. *J. Organomet. Chem.* **1983**, *258*, C12.

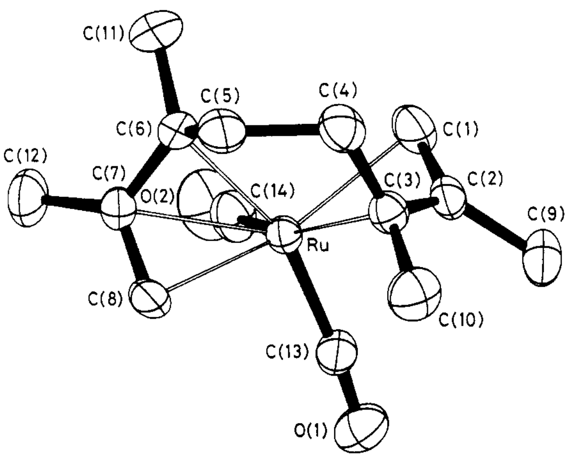

Figure 1. Geometry of the $Ru(CO)_2(\eta^3:\eta^3$-tetramethyloctadienediyl) molecule (ORTEP diagram with 30% ellipsoids). Hydrogen atoms are omitted for clarity. The Ru–C(3) and Ru–C(2) bonds are superimposed in this drawing.

Table IV. Interatomic Angles (deg) and Esd's for 2

C(1)–C(2)–C(3)	118.8 (3)	C(5)–C(6)–C(7)	119.8 (3)
C(1)–C(2)–C(9)	117.5 (3)	C(5)–C(6)–C(11)	112.7 (4)
C(3)–C(2)–C(9)	123.4 (3)	C(7)–C(6)–C(11)	120.9 (3)
C(2)–C(3)–C(4)	119.6 (3)	C(6)–C(7)–C(8)	118.1 (3)
C(2)–C(3)–C(10)	120.2 (3)	C(6)–C(7)–C(12)	122.2 (3)
C(4)–C(3)–C(10)	113.0 (3)	C(8)–C(7)–C(12)	119.6 (3)
C(3)–C(4)–C(5)	111.6 (3)	Ru–C(13)–O(1)	174.9 (3)
C(4)–C(5)–C(6)	111.5 (3)	Ru–C(14)–O(2)	176.1 (3)
C(1)–Ru–C(3)	64.7 (1)	C(3)–Ru–C(13)	98.0 (1)
C(1)–Ru–C(6)	92.8 (1)	C(3)–Ru–C(14)	157.8 (1)
C(1)–Ru–C(8)	152.6 (2)	C(6)–Ru–C(8)	64.4 (1)
C(1)–Ru–C(13)	108.0 (1)	C(6)–Ru–C(13)	156.4 (1)
C(1)–Ru–C(14)	93.2 (1)	C(6)–Ru–C(14)	100.6 (1)
C(3)–Ru–C(6)	80.4 (1)	C(8)–Ru–C(13)	92.5 (1)
C(3)–Ru–C(8)	95.3 (1)	C(8)–Ru–C(14)	105.2 (1)
		C(13)–Ru–C(14)	89.7 (2)

sequentially from C(1). Crystal data, atomic positional parameters, and relevant bond lengths and angles are presented in Tables I–IV.

The molecule possesses a noncrystallographic C_2 axis which is defined by the vector connecting the ruthenium atom to the midpoint of C(4)–C(5). The coordination polyhedron about ruthenium is best described by the atoms C(1), C(3), C(6), C(14), C(13), and C(8) which define a distorted octahedron. The octahedral angles are included in Table IV, and the major distortions result from the small "bite" angle subtended by the two allyl groups (64.5° mean). The CO ligands are mutually cis and the termini of the organic ligand mutually trans.

The six Ru–C(allyl) distances range from 2.205 (3) to 2.316 (3) Å with the Ru–C(3) and Ru–C(6) bonds significantly longer than the remaining four by 0.05–0.11 Å. This may arise from the natural bonding requirements of the ligand or, alternatively, may be ascribed to the trans relationship of C(3) and C(6) to the two carbonyl groups.[17] The dihedral angles between an allyl plane (C(1)C(2)C(3) or C(6)C(7)C(8)) and the plane defined by the ruthenium atom and the outer allyl C atoms (C(1)C(3)Ru or C(6)C(8)Ru) are 107.9° and 106.8°, respectively. These values together with the C–C distances (1.40 Å mean) and the internal C–C–C angles (118.5° mean) within the allyl groups may be considered typical of transition-metal η^3-allyl coordination.[18,19]

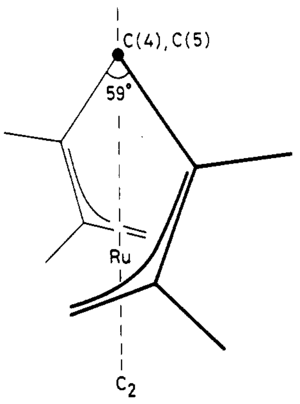

Figure 2. Schematic Newman-like projection of the organic ligand in 2 down the C(4)–C(5) bond.

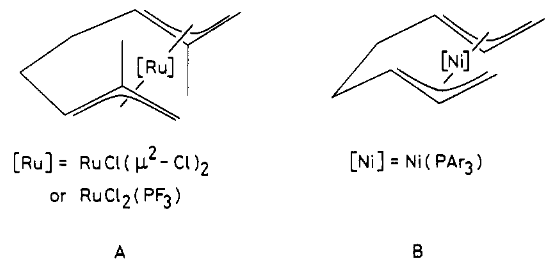

Figure 3. Previously observed configurations of $\eta^3:\eta^3$-octadienediyl ligands.

The four methyl substituents on the two allyl groups all deviate from the allyl planes and bend slightly toward the metal atom. This deviation is characterized by the angle between the allyl planes and the appropriate C–C vector and equals 4.5° (mean) for the methyls C(9) and C(12) and 6.5° (mean) for the methyls C(10) and C(11). The latter are syn substituted on the allyl carbon atoms C(3) and C(6). The anti sites on C(3) and C(6) are occupied by the methylene chain carbon atoms C(4) and C(5) which form the spine of the organic ligand. Both C(4) and C(5) bend appreciably away from the ruthenium atom by 40 (3)° and 37 (2)° as defined by the C(4)–C(3)–C(2)–C(1) and C(5)–C(6)–C(7)–C(8) torsion angles. This leads to Ru···C(4) and Ru···C(5) distances of 3.078 (3) and 3.076 (3) Å, respectively. With the usual caveat on hydrogen atom location the protons on C(1) and C(8) show related deviations from the allyl planes, H_{syn} atoms bending slightly toward (0.1 Å) and H_{anti} atoms appreciably away from the ruthenium atom (0.5 Å from allyl plane).

The C(3)–C(4)–C(5)–C(6) torsion angle of 59 (3)° effectively sets, and is therefore presumably dictated by, the relative conformation of the allyl groups about the ruthenium atom. This is illustrated schematically in Figure 2. The C(4)–C(5) distance of 1.511 (5) Å is not significantly different from that of the other single C–C bonds in the molecule. The dihedral angle between the allyl planes is 84.6°.

Ligand Configuration in 2 and 4. An interesting feature of the structure of 2 is the occupation of the anti sites on C(3) and C(6) by the methylene chain. In the related $[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})]_2$[9] and $RuCl_2(PF_3)(\eta^3:\eta^3\text{-}C_{10}H_{16})$[20] the methylene chain of the octadienediyl ligand occupies the alternative syn sites (Figure 3A). Similarly, in the series of $NiL(\eta^3:\eta^3$-octadienediyl) species studied by Wilke et al.[3] the structural type shown in Figure 3B has

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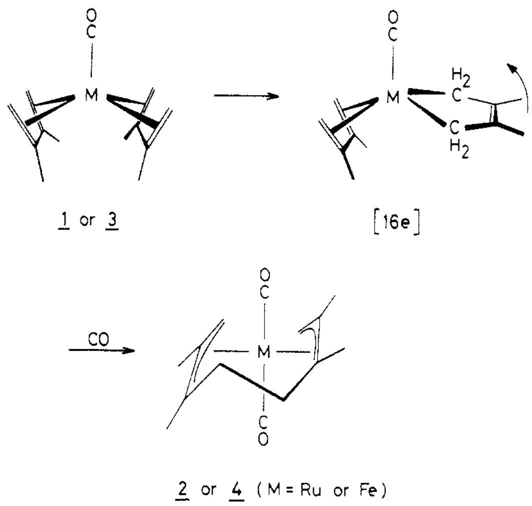
[17] A similar trans influence has been observed in the structure of $Ru(P(OMe)_3)_2(2\text{-}MeC_3H_4)_2$ for carbon atoms trans to the phosphites (Marsh, R. A.; Howard, J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1973**, 788).

[18] Clarke, H. L. *J. Organomet. Chem.* **1974**, *80*, 155.

[19] Kaduk, J. A.; Poulos, A. T.; Ibers, J. A. *J. Organomet. Chem.* **1977**, *127*, 245.

[20] Hitchcock, P. B.; Nixon, J. F.; Sinclair, J. *J. Organomet. Chem.* **1975**, *86*, C34.

Scheme I



been proposed from the NMR spectra. The methylene chain is again syn.

The unusual anti position of the methylene chain in **2** (and presumably **4**) may result from thermodynamic factors. For example, it may give rise to an optimal relative orientation of the allyl groups about an $M(CO)_2$ center and/or minimize steric congestion between the four methyl groups. It is not certain, however, that the carbonylation reactions forming **2** and **4** are subject to thermodynamic product control. The observed products may equally result from kinetic control where configurational changes of the chelating bis(allyl), once formed, cannot occur. Such a hypothesis is consistent with the observed nonfluxionality of **2** and **4** in solution (no syn–anti proton exchange at +80 °C) and the absence of other isomers in the crude products.

If subsequent rearrangement of the chelating bis(allyl) is ruled out, the observed ligand configuration reflects the intimate mechanism of the coupling reaction. The anti position of the methylene chain therefore becomes particularly noteworthy for the retention of the cisoid conformation of the diene remnants. Two mechanisms can be advanced which enforce the retention of the cisoid diene conformation. The first would involve a direct $\eta^4 + \eta^4$ coupling mechanism. However, since the expected ground state of the $M(CO)(\eta^4\text{-}C_6H_{10})_2$ precursors **1** and **3** is tetragonal-pyramidal C_{2v} (in common with all other structurally characterized $M(CO)(diene)_2$ species),[21-24] a relative 90° rotation of the dienes prior to coupling is required. It is not clear why such a rotation should occur, although in metallaborane chemistry a related 90° rotation of η^4-bonded ligands has been observed on effective two-electron addition (16-electron $[Ni(B_{10}H_{12})_2]^{2-}$ vs. 18-electron $[Zn(B_{10}H_{12})_2]^{2-}$).[25,26] The *nido*-$B_{10}H_{12}^{2-}$ ligand is isolobal with *cis*-dienes.[27] The addition of CO to **1** and **3** prior to coupling could similarly be considered an effective two-electron addition, although unless the reaction is concerted, a 20-electron intermediate would result. The second possible mechanism features a 16-electron metallacyclic intermediate which collapses stereospecifically as illustrated in the Scheme I. Intermediates of this type were first invoked by Ittel[28] to explain the nondissociative isomerization of $Fe(P(OR)_3)(\eta^4\text{-isoprene})_2$.

Conclusion

In eq 2 a new reaction type has been proposed and the first examples have been reported on CO addition to $M(CO)(\eta^4\text{-}2,3\text{-dimethylbutadiene})_2$ (M = Fe, Ru). At present it is uncertain if these diene coupling reactions are a general feature of $ML(diene)_2$ chemistry. The reaction is not, however, confined to 2,3-dimethylbutadiene since we have recently observed the formation of the known $Ru(CO)_2(\eta^3{:}\eta^3\text{-}C_{12}H_{16})$[7] on CO addition to $Ru(CO)(\eta^4\text{-}1,3\text{-cyclohexadiene})_2$.[29]

Doubt on the generality of the diene coupling reaction is cast by the previous reports of attempted ligand addition to $ML(diene)_2$ complexes. Hence, $Ru(PPh_3)(\eta^4\text{-butadiene})_2$ and $Fe(CO)(\eta^4\text{-butadiene})_2$ have been reported to react with a variety of phosphines to produce $ML_3(\eta^4\text{-}C_4H_6)$ type complexes in high yield.[30] Alternatively, Ittel et al.[28] have noted that $Fe(P(OMe)_3)(\eta^4\text{-isoprene})_2$ is not susceptible to further phosphite addition. Furthermore, the spectroscopic identification of several $ML_2(\eta^4\text{-diene})(\eta^2\text{-diene})$ complexes (M = Fe, L = $P(OR)_3$; M = Ru, L = PPh_3) indicates that such species may be long-lived and stable with respect to diene coupling.[28,31,32] Investigations aimed at observing further examples of diene coupling reactions of the above type are in progress.

Experimental Section

General Comments. Unless otherwise stated all manipulations were carried out under argon using standard Schlenk techniques. Solvents were distilled over Na and degassed before use. 2,3-Dimethylbutadiene (Fluka AG) was distilled over CaH_2. Red crystals of carbonylbis(η^4-2,3-dimethylbutadiene)iron (**3**) were obtained by low-temperature photolysis of $Fe(CO)_5$ (Fluka AG) following a literature procedure.[10] Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer (pentane solutions) and calibrated with polystyrene film. NMR spectra were recorded on a Bruker WH-360 FT spectrometer (^1H, 360; ^{13}C, 90.55 MHz; D signal of solvent as lock; Me_4Si as internal reference). Mass spectra were recorded on a Hewlett-Packard 5980 GC–MS spectrometer in electron-ionization mode. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, West Germany, and by the Mikrolabor of the ETH, Zürich, Switzerland.

Preparation of $Ru(CO)(\eta^4\text{-}C_6H_{10})_2$ (1). A vapor synthesis plant G.V. Planar Ltd. (VSP 500) was used, and details have been given by us elsewhere.[1] In a typical experiment, ca. 1 g of Ru atoms (ca. 10 mmol) was cocondensed with ca. 30 mL of 2,3-dimethylbutadiene (ca. 300 mmol) at −196 °C over a period of 2 h. The condensate was then allowed to warm to −20 °C under a constant pressure of 1 atm of CO. The orange-brown condensate was extracted from the reactor with cold THF (300 mL) and immediately filtered through dry Florisil. The solvent was removed under reduced pressure without heating, and cold pentane (200 mL) was added to the oil obtained. After the solution was stirred over activated charcoal (2 g) for 5 min, filtration gave a yellow-orange solution. Concentration and cooling to −78 °C gave **1** as moderately air-stable pale orange microcrystalline plates (720

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mg, 25%). Once pure this compound can be satisfactorily sublimed at 50 °C (10^{-4} mbar), and yellow microcrystals are obtained: mp 65 °C dec; IR 1993 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 1.82 (d, J_{gem} = 1.3 Hz, 4 H, H trans to C(2)–C(3)), 1.71 (s, 12 H, Me), 0.23 (d, 4 H, H cis to C(2)–C(3)); ^{13}C NMR ($CDCl_3$) δ 218.1 (s, CO), 92.4 (s, C(2), C(3)), 36.0 (t, J_{CH} = 156 Hz, C(1), C(4)), 17.6 (q, J_{CH} = 127 Hz, Me); MS (70 eV), *m/e* relative to ^{102}Ru (relative intensity) 294 [M^+] (23), 266 (84), 260 (100), 182 (68), 102 (22). Anal. Calcd for $C_{13}H_{20}ORu$: C, 53.22; H, 6.87. Found: C, 53.37; H, 6.79.

Preparation of $Ru(CO)_2(\eta^3{:}\eta^3\text{-}C_{12}H_{20})$ (2). Complex 1 (0.3 g, 1.0 mmol) was dissolved in THF (100 mL) and the yellow solution refluxed under CO (1 atm) for 90 min without any apparent color change. The solvent was then removed in vacuo, and the crude product was purified by sublimation (50 °C (10^{-4} mbar)) onto a cold finger held at −30 °C. This produced pure 2 (130 mg, 40%) as a pale yellow microcrystalline powder: mp 61 °C; IR 2010, 1947 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 3.37 and 2.87 (each d, J_{gem} = 1.1 Hz, 4 H, $H_2C(1)$, $H_2C(8)$), 2.14 and 1.60 (each s, 12 H, Me), 1.74 and 1.50 (each d, J_{gem} = 8.5 Hz, 4 H, $H_2C(4)$, $H_2C(5)$); ^{13}C NMR ($CDCl_3$) δ 203.3 (s, CO), 115.9 and 86.7 (each s, C(2), C(3), C(6), C(7)), 42.4 (t, J_{CH} = 125 Hz, C(4), C(5)), 40.7 (t, J_{CH} = 155 Hz, C(1), C(8)), 23.6 and 22.3 (each q, J_{CH} = 125 Hz, Me); MS (70 eV), *m/e* (relative intensity) 322 [M^+] (29), 294 (21), 266 (96), 260 (100), 182 (51), 102 (15). Anal. Calcd for $C_{14}H_{20}O_2Ru$: C, 52.32; H, 6.27. Found: C, 52.34; H, 6.44.

Preparation of $Fe(CO)_2(\eta^3{:}\eta^3\text{-}C_{12}H_{20})$ (4). Complex 3 (3.0 g, 12 mmol) was dissolved in THF (100 mL) and the orange solution refluxed under CO (1 atm) for 21 h. The solvent was then removed in vacuo giving a black oil which was extracted with pentane (200 mL). After the pentane extract was stirred with activated charcoal (2 g), filtration gave a yellow-green solution which was concentrated to an intensely colored oil. Chromatography on a 200 × 2 cm column packed with silica gel using pentane as eluent gave a first fraction identified as $Fe(CO)_3$-(η^4-2,3-dimethylbutadiene) (1.4 g, 53%) by spectroscopic comparison with an authentic sample. Continued elution produced a second fraction which yielded pure 4 as an orange-red oil (0.63 g, 19%) on sublimation (20 °C (10^{-4} mbar)). Traces of an unidentified dark green iron cluster were eluted with THF. 4: IR 1987, 1930 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 3.22 and 2.70 (each d, J_{gem} = 1.3 Hz, 4 H, $H_2C(1)$, $H_2C(8)$), 2.05 and 1.54 (each s, 12 H, Me), 1.75 and 1.39 (each d, J_{gem} = 8.1 Hz, 4 H, $H_2C(4)$, $H_2C(5)$); ^{13}C NMR ($CDCl_3$) δ 217.5 (s, CO), 110.0 and 91.2 (each s, C(2), C(3), C(6), C(7)), 46.8 (t, J_{CH} = 157 Hz, C(1), C(8)), 42.2 (t, J_{CH} = 125 Hz, C(4), C(5)), 23.6 and 22.4 (each q, J_{CH} = 126 Hz, Me); MS (70 eV), *m/e* (relative intensity) 276 [M^+] (5), 248 (11), 220 (49), 138 (100). Anal. Calcd for $C_{14}H_{20}FeO_2$: C, 60.89; H, 7.30. Found: C, 61.47; H, 7.30.

Carbonylation reactions of 2 and 4 were attempted. In separate experiments 2 (0.12 g, 0.65 mmol) and 4 (0.10 g, 0.36 mmol) were dissolved in THF (12 mL) and the solution was heated at 60 °C for 48 h in an autoclave charged with CO (100 atm). In each case, IR spectra (pentane) indicated that no new carbonyl species had been formed and on sublimation 2 and 4 were recovered unchanged (90 and 65%, respectively).

X-ray Diffraction Study of $Ru(CO)_2(\eta^3{:}\eta^3\text{-}C_{12}H_{20})$ (2). Suitable crystals of 2 were first obtained by slow vacuum sublimation in a sealed tube held at 30 °C. A well-formed single crystal of approximate dimensions 0.21 × 0.17 × 0.15 mm was mounted on a Syntex $P2_1$ autodiffractometer. Unit cell parameters were determined from 25 accurately centered reflections with 2θ values greater than 40°. The Mo $K\alpha_1$ and $K\alpha_2$ were well separated, and the parameters were calculated on the basis of $K\alpha_1$ (λ = 0.709 26 Å). Information on data collection appears in Table I. All 1964 unique reflections were corrected for absorption (Gaussian integration), Lorentz, and polarization effects. Subsequent structure solution and refinement calculations were performed with the X-ray 72 system of programs.[34] Atomic scattering factors calculated by Cromer and Mann[35] were assigned to the non-hydrogen atoms. For hydrogen atoms the values calculated by Stewart et al.[36] were introduced in the structure factor calculations. Anomalous dispersion corrections[37] were applied to the Ru atoms which were located from a Patterson map. The remaining heavy atoms could be identified on successive Fourier maps. A difference Fourier synthesis resulting from an anisotropic refinement of the non-hydrogen atoms revealed all 20 hydrogen atoms. Subsequent refinement with isotropic thermal coefficients for hydrogen atoms gave the final R = 1.8%, R_w = 1.0%, and GOF = 2.78 for 234 variables refined against 1843 reflections (1754 with $I > 3\sigma(I)$ and 89 less than with $F_o > F_c$). The function minimized during full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2$. Final positional parameters are shown in Table II; anisotropic thermal parameters, distances and angles including hydrogen atoms, least-squares planes data, and a listing of observed and calculated structure factor amplitudes are deposited in Table II-S (supplementary material).

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Registry No. 1, 92467-55-5; 2, 98170-33-3; 3, 38117-69-0; 4, 98170-34-4; $Fe(CO)_3(\eta^4\text{-}C_6H_{10})$, 31741-56-7; $Ru(CO)_2(\eta^3{:}\eta^3\text{-}C_{12}H_{16})$, 41684-44-0; $Ru(CO)(\eta^4$-1,3-cyclohexadiene), 92468-32-1; Ru, 7440-18-8; 2,3-dimethylbutadiene, 513-81-5.

Supplementary Material Available: Table II-S, a listing of observed and calculated structure factor amplitudes, anisotropic thermal parameters, distances and angles including hydrogen atoms, and least-squares plane data (15 pages). Ordering information is given on any current masthead page.

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