Regio- and Diastereoselective C–C Coupling of Two η^3-Allyl Fragments on a Tetranuclear Ruthenium Chain Complex[1]

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Summary: Thermolysis of $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}t\text{-}Bu]$ (**1**), which contains a σ-N, μ_2-η^3-bonded allylimine ligand, in refluxing *n*-octane for 24 h yields the novel tetranuclear chain complex $Ru_4(CO)_{10}[(CH_2C{=}C(H)C(H){=}N\text{-}t\text{-}Bu)_2]$ (**2**) in about 40% yield. The X-ray crystal structure of **2** has been solved. Crystals of **2** are triclinic, with space group $P\bar{1}$, $Z = 2$, and cell constants $a = 9.279$ (1) Å, $b = 13.647$ (1) Å, $c = 13.981$ (1) Å, $\alpha = 60.84$ (1)°, $\beta = 88.26$ (1)°, and $\gamma = 84.90$ (1)°. A total of 5636 reflections were used in the refinement, which resulted in a final *R* value of 0.028 ($R_w = 0.039$). Compound **2** contains a multidentate 1,10-di-*tert*-butyl-1,10-diazadeca-1,3,7,9-tetraene-4,7-diyl ligand that is formed by completely regio- and diastereoselective tail-to-tail coupling of two allyl fragments on the ruthenium core. The 66-electron compound **2** represents the first acyclic tetranuclear chain complex stabilized by a multidentate ligand bonded to all four metal centers.

Carbon–carbon coupling reactions on small transition-metal units are of substantial interest because they may serve as models for such processes taking place on dissolved complex metallic catalysts in homogeneously catalyzed reactions and on the active sites of heterogeneous catalysts.[2] Although C–C coupling between η^3-allyl groups has been observed for a number of group 9 and 10 metals (i.e. Co, Ni, Pd),[2a–c] it has, to our surprise, not been found on a ruthenium carbonyl (cluster) unit so far, despite the variety of mono- and bis(η^3-allyl)ruthenium complexes known.[3] In this paper we wish to report on the synthesis and molecular structure of a novel tetranuclear ruthenium chain complex containing a 1,10-di-*tert*-butyl-1,10-diazadeca-1,3,7,9-tetraene-4,7-diyl (*t*-Bu-DAT) ligand, which is formed by completely regio- and diastereoselective tail-to-tail coupling of two η^3-allyl fragments on the ruthenium core.

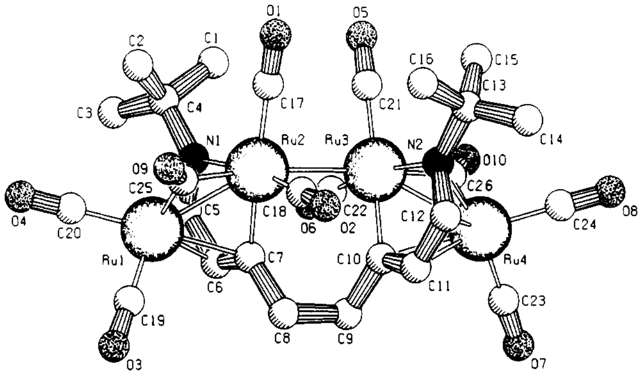

Figure 1. Molecular view of $Ru_4(CO)_{10}[(CH_2C{=}C(H)C(H){=}N\text{-}t\text{-}Bu)_2]$ (**2**), with numbering scheme. Relevant bond lengths (Å): Ru(1)–Ru(2) = 2.6940 (6), Ru(2)–Ru(3) = 2.8833 (5), Ru(3)–Ru(4) = 2.6858 (6), Ru(1)–N(1) = 2.226 (3), Ru(1)–C(5) = 2.249 (4), Ru(1)–C(6) = 2.288 (4), Ru(1)–C(7) = 2.309 (4), Ru(1)–C(25) = 2.067 (4), Ru(2)–N(1) = 2.212 (4), Ru(2)–C(7) = 2.084 (4), Ru(2)–C(25) = 2.098 (4), Ru(3)–N(2) = 2.220 (5), Ru(3)–C(10) = 2.070 (4), Ru(3)–C(26) = 2.120 (4), Ru(4)–N(2) = 2.234 (3), Ru(4)–C(10) = 2.327 (4), Ru(4)–C(11) = 2.289 (4), Ru(4)–C(12) = 2.252 (5), Ru(4)–C(26) = 2.071 (5), N(1)–C(5) = 1.355 (5), C(5)–C(6) = 1.414 (6), C(6)–C(7) = 1.390 (6), C(7)–C(8) = 1.508 (6), C(8)–C(9) = 1.530 (6), C(9)–C(10) = 1.517 (6), C(10)–C(11) = 1.407 (6), C(11)–C(12) = 1.406 (7), C(12)–N(2) = 1.359 (6). Relevant bond angles (deg): Ru(1)–Ru(2)–Ru(3) = 137.38 (2), Ru(2)–Ru(3)–Ru(4) = 138.68 (2), C(7)–C(8)–C(9) = 110.3 (3), C(8)–C(9)–C(10) = 109.4 (3).

In the course of our study, aimed at cyclometalation of 1-aza-1,3-dienes and formation of azametallacyclopentadiene systems, a number of interesting di-,[4] tri-,[5] and tetranuclear[6] ruthenium compounds, containing an isomerized or dehydrogenated azadiene ligand that is part of a four- or five-membered azaruthenacycle, have been synthesized, the reactivity of which is currently being investigated.

Thermolysis of one of these, the dinuclear $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}t\text{-}Bu]$ (**1**),[4] which contains a σ-N, μ_2-η^3-bonded allylimine ligand, in refluxing *n*-octane (bp 125 °C) for 24 h under an inert atmosphere produces the new tetranuclear cluster $Ru_4(CO)_{10}[(CH_2C{=}C(H)C(H){=}N\text{-}t\text{-}Bu)_2]$ ($Ru_4(CO)_{10}[t\text{-}Bu\text{-}DAT]$; **2**) in a yield of about 40% (Scheme I).[7] This conversion is most likely initiated

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[1] Reactions of Metal Carbonyl Complexes with Monoazadienes. 8. For earlier parts see refs 4–6 and 14.

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[7] Synthesis of **2**: A yellow solution of $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}t\text{-}Bu]$[2a] (**1**; 1 mmol) in *n*-octane (40 mL) was heated at reflux for 24 h under an atmosphere of dry nitrogen. When the mixture was cooled to room temperature, a dark brown precipitate of $Ru_4(CO)_{10}[(CH_2C{=}C(H)C(H){=}N\text{-}t\text{-}Bu)_2]$ (**2**) was formed, which was isolated by filtration. The crude product was dissolved in dichloromethane and filtered over a gel of silica, affording pure **2** (ca. 40% yield). Hazel brown crystals of **2** were obtained by slow evaporation of pentane into a concentrated dichloromethane solution of **2**.

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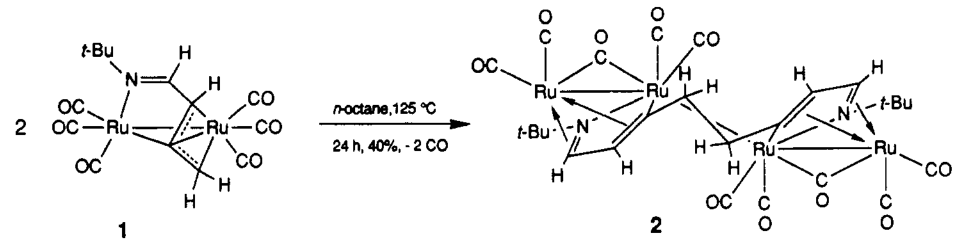
Scheme I



1 2

by thermally induced loss of a CO ligand from 1, followed by dimerization of the thus-formed transient coordinatively unsaturated [$Ru_2(CO)_5(CH_2CC(H)C(H){=}N\text{-}t\text{-}Bu)$] species or association with another molecule of 1. The resulting tetranuclear ruthenium frame serves as a template for the consecutive regioselective reductive C–C coupling of the two η^3-allyl fragments, giving rise to the formation of a 1,5-diene unit.

As 1 consists of a mixture of two enantiomers, the title reaction may in principle result in the formation of two diastereomers of 2.[8] However, both in solution (^{1}H and ^{13}C{^{1}H} NMR)[9] and in the solid state (X-ray) only one diastereomer of 2 is observed.[10] A ^{1}H NMR spectrum of a crude reaction mixture also showed the sole presence of this diastereomer of 2. Thus, diastereospecific formation of 2 must have taken place by chiral recognition between two *homochiral* molecules of [$Ru_2(CO)_n(CH_2CC(H)C(H){=}N\text{-}t\text{-}Bu)$] ($n$ = 5, 6), which provide, as indicated by inspection of molecular models, a better mutual fit than two *heterochiral* molecules.

The structure of 2 has been elucidated by X-ray crystallography.[11] A PLUTO drawing of one of the two enantiomers present in the centrosymmetric unit cell is presented in Figure 1.

The molecular structure of 2 possesses noncrystallographic C_2 symmetry, with the 2-fold axis running through the midpoints of the central Ru(2)–Ru(3) bond and the new C(8)–C(9) bond. The (σ-N,σ-C,η^2-C=C,η^2-C=N)$_2$-bonded t-Bu-DAT ligand donates 14 electrons to the cluster core while the 8 terminal and 2 asymmetrically bridging CO ligands donate 20 electrons. Consequently, 2 contains a total of 66 cluster electrons, for which the presence of three metal–metal bonds is predicted.[12] The intermetallic distances in 2 (Ru(1)–Ru(2) = 2.694 (6) Å, Ru(2)–Ru(3) = 2.8833 (5) Å, Ru(3)–Ru(4) = 2.6858 (6) Å) indicate the presence of three normal single ruthenium–ruthenium bonds, from which it may be concluded that this tetranuclear chain complex is electron-precise. The intermetallic bond angles deviate considerably from linearity; i.e., the Ru(1)–Ru(2)–Ru(3) and Ru(2)–Ru(3)–Ru(4) angles amount to 137.38 (2) and 138.68 (2)°, respectively.[13] This is probably caused by the reduced conformational freedom of the tetraruthenium moiety due to the coupling of the carbon fragments at C(8)–C(9) in the t-Bu-DAT ligand. The intermetallic angles in a related tetranuclear ruthenium chain complex, $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$, in which two separate azaruthenacycles are present, amount to 174.550 (16)°.[6] The new central C(8)–C(9) bond connecting the two aza dien-4-yl subunits of the t-Bu-DAT ligand and the sp^3 C(8) and C(9) atoms show normal geometric features. The σ-N,σ-C,η^2-C=C,η^2-C=N coordination of the azadien-4-yl subunits in 2 is reminiscent of the 7e coordination mode of this ligand as has been found for several di-, tri-, and tetranuclear complexes.[5,6,14] The overall geometry of the rigid cluster is a result of the snakelike winding of the t-Bu-DAT ligand around the metal frame. Compound 2 represents the first acyclic tetranuclear transition-metal complex that is stabilized by a multidentate ligand, bonded to all four metal centers.

The ^{1}H and ^{13}C{^{1}H} NMR data[9] for 2 in CDCl$_3$ solution are consistent with the molecular structure in the solid state. The AB pattern at δ 3.44 and 2.54 ppm in the ^{1}H NMR spectrum with a geminal coupling of 7.5 Hz is in agreement with the conversion of the methylene groups of the two η^3-allyl moieties into an ethane-1,2-diyl unit.

Complex 2 is thermally rather stable; only slight decomposition takes place when it is refluxed in toluene over a period of 72 h. Apparently, stabilization of 2 is reached by octadentate bonding of the t-Bu-DAT ligand to the metal core. Furthermore, 2 could not be reconverted into 1 by refluxing 2 in toluene under a CO atmosphere. This

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(8) Although 1 contains two and 2 contains four stereogenic ruthenium centers, these are pairwise related. Hence, 1 consists of one pair of enantiomers (one diastereomer) and 2 might consist of two pairs of enantiomers (two diastereomers), of which only one pair is observed.

(9) Spectroscopic and analytical data for 2: IR (ν(CO), in cm^{-1}) 2042 (vw), 2018 (vs), 1995 (m), 1962 (m br), 1840 (w br) in CH_2Cl_2; 2038 (vw), 2002 (vs), 1986 (s), 1968 (s), 1958, (s), 1942 (s), 1936 (s), 1848 (m), 1841 (s) in KBr disk; ^{1}H NMR (100 MHz, $CDCl_3$, 297 K, δ in ppm, J in Hz) 7.48 (d, ^3J = 2.0, N=C*H*), 6.88 (d, ^3J = 2.0, C=C*H*), 3.44 (d, ^2J = 7.5, CCH*H*), 2.54 (d, ^2J = 7.5, CC*H*H), 1.22 (s, NC(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR (25.0 MHz, $CDCl_3$, 263 K, δ in ppm) 203.8, 201.7, 201.4 (*C*O's, CH$_3$*C*=CH), 121.1 (N=*C*H), 111.1 (C=*C*H), 62.6 (C*C*H$_2$), 57.9 (N*C*(CH$_3$)$_3$), 23.0 (NC(*C*H$_3$)$_3$); FD-mass found m/e 928 (calcd M_r = 930; based on ^{101}Ru). Anal. Found (calcd) for $C_{26}H_{26}N_2O_{10}Ru_4$: C, 33.18 (33.55); H, 2.67 (2.82); N, 3.24 (3.01).

(10) The other, unobserved diastereomer of 2 would be built up of two heterochiral dinuclear units and would formally possess C_s symmetry, with the two unsaturated azadien-4-yl subunits bonded to the same face instead of to opposite faces of the metal core as in the isolated diastereomer.

(11) Crystal data for 2: $C_{26}H_{26}N_2O_{10}Ru_4$, M_r = 930.78, brownish plate-shaped crystal (0.1 × 0.3 × 0.5 mm), triclinic, space group $P\bar{1}$, a = 9.279 (1) Å, b = 13.647 (1) Å, c = 13.981 (1) Å, α = 60.84 (1)°, β = 88.26 (1)°, γ = 84.90 (1)°, V = 1539.8 (3) Å^3, Z = 2, d_{calcd} = 2.007 g cm^{-3}, $F(000)$ = 904, μ(Mo Kα) = 19.4 cm^{-1}. Independent reflections ($\theta < 28.2°$; $\omega/2\theta$ scan; $\Delta\omega = 0.55 + 0.35 \tan\theta$; T = 295 K) were measured on an Enraf-Nonius CAD4F diffractometer (Mo Kα; Zr-filtered; 0.71073 Å). Data were corrected for Lp and absorption (DIFABS). The structure was solved with heavy-atom methods and refined by full-matrix anisotropic least squares (SHELX76) to R = 0.028 (R_w = 0.039; S = 1.09; $\omega^{-1} = \sigma^2(F)$; 409 parameters; 5636 reflections with $I > 2.5\sigma(I)$). Hydrogen atoms were introduced on calculated positions and refined on their carrier atoms with three common isotropic thermal motion parameters. A final difference Fourier map showed no residual densities outside 0.7 and −0.9 e Å^{-3} (near Ru atoms).

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indicates that the new central C–C bond of the *t*-Bu-DAT ligand is thermally resistant toward homo- and heterolytic fission.

The presented concept of selective dimerization of chiral metal units and preorganization of carbon fragments followed by C–C coupling might well be extended to the directed synthesis of functionalized dienes on small transition-metal clusters.

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Registry No. 1, 123083-55-6; 2, 131704-20-6.

Supplementary Material Available: Tables of fractional coordinates of all atoms, bond distances and angles, and anisotropic thermal motion parameters for 2 and an ORTEP diagram of 2 showing 30% probability ellipsoids (7 pages); a listing of observed and calculated structure factor amplitudes (42 pages). Ordering information is given on any current masthead page.

Cycloalkyne Ligands Formed by the Coupling of Polymethylene-Bridged Alkylidynes: $L_nM{\equiv}C(CH_2)_nC{\equiv}ML_n \rightarrow L_{2n}M_2(\mu\text{-}C_2(CH_2)_n)$

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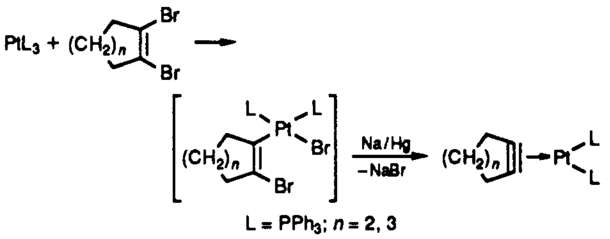
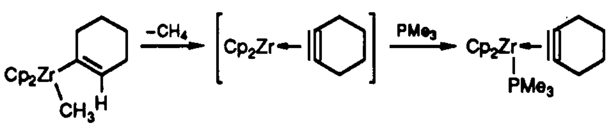
Summary: Polymethylene-bridged alkylidyne complexes $(t\text{-BuO})_3W{\equiv}C(CH_2)_nC{\equiv}W(O\text{-}t\text{-Bu})_3$ (I) have been prepared from the reactions between $W_2(O\text{-}t\text{-Bu})_6(M{\equiv}M)$ and the dinitriles $N{\equiv}C(CH_2)_nC{\equiv}N$, where n = 3–6, in hexane. Addition of carbon monoxide to hydrocarbon solutions of I leads to the formation of the cycloalkyne adducts $(t\text{-BuO})_6W_2(\mu\text{-}C_2(CH_2)_n)(CO)$ (II) for n = 4, 5 but not for n = 3, 6. These results are discussed in terms of the stereochemical requirements for the reversible reaction $2L_nM{\equiv}CR \rightleftarrows L_{2n}M_2(\mu\text{-}C_2R_2)$.

Cycloalkynes $C_2(CH_2)_n$ with small rings (n = 3–5) are kinetically too labile to be isolated as pure compounds.[1] They may be stabilized by coordination to metal atoms, and three routes, shown in eqs 1–3, have been developed to such complexes.[2-4] Two are similar in that they start from cycloalkenylmetal precursors, and the third involves closure of the ring in a preformed acyclic alkyne complex by carbon–carbon bond formation away from the coordinated triple bond.

We describe here a new synthetic approach for the generation of certain cycloalkyne ligands based on the coupling of two linked metal–alkylidyne moieties. This coupling reaction takes advantage of the equilibrium shown in eq 4, which is sensitive to both steric and electronic effects.[5]



(1)



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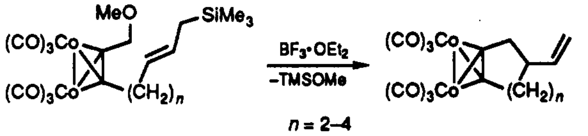

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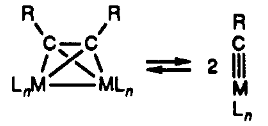

(4)

In the present study the dialkylidyne compounds $(t\text{-BuO})_3W{\equiv}C(CH_2)_nC{\equiv}W(O\text{-}t\text{-Bu})_3$ (I), where n = 3–6, were prepared from the reaction shown in eq 5, a reaction based on chemistry developed by Schrock.[6] The tungsten nitride

$$2W_2(O\text{-}t\text{-Bu})_6(M{\equiv}M) + N{\equiv}C(CH_2)_nC{\equiv}N \xrightarrow[\text{hexane}]{22\ ^\circ\text{C}} 2(t\text{-BuO})_3W{\equiv}N + \underset{\text{I}}{(t\text{-BuO})_3W{\equiv}C(CH_2)_nC{\equiv}W(O\text{-}t\text{-Bu})_3} \quad (5)$$

that forms is polymeric, is insoluble in hexane, and can be removed from the reaction mixture by filtration.[7] Re-

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