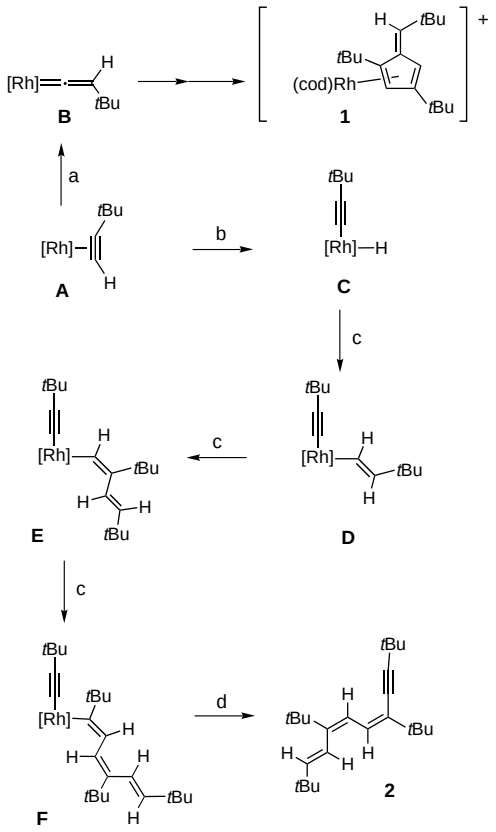
Rhodium-Promoted Linear Tetramerization and Cyclization of 3,3-Dimethylbut-1-yne**

Andrew D. Burrows, Michael Green,* John C. Jeffery, Jason M. Lynam, and Mary F. Mahon

Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

Following the early work of Reppe et al.[1] and continuing throughout the development of modern organotransition metal chemistry[2] there has been a sustained interest in the reactions of alkynes with transition metal centers. Recently attention has focused on both linear oligomerization reactions[3–5] and on the trimerization of alkynes to form fulvenes,[6–8] potential synthons for substituted cyclopentadienyl ligands.[7, 9]

We had earlier found[6] that reaction of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (cod = cycloocta-1,5-diene) with tBuC$_2$H and $AgPF_6$ in CH_2Cl_2 led to the selective formation of the cationic fulvene complex **1** (Scheme 1), from which the free fulvene could be readily displaced by acetonitrile. In seeking to establish a catalytic version of this chemistry we added tBuC$_2$H to a solution of the labile complex $[Rh(NCMe)_2(cod)][BF_4]$[10] in dichloromethane, but were surprised to observe that there was no reaction at 40 °C. However, using the same reactants with tetrahydrofuran (THF) as the solvent, in which the more labile complex $[Rh(thf)_2(cod)][BF_4]$ could be formed by ligand displacement, the color of the reaction mixture changed rapidly (0.5 h, 50 °C) from yellow to deep red. Following removal of the solvent an orange solid was isolated, which showed in its ^{1}H NMR spectrum resonances corresponding to a single organic product in addition to $[Rh(cod)]^+$ species. The organic compound was purified by column chromatography (silica gel; diethyl ether) and recrystallization (acetone/ethanol, 1/1) to give crystals of **2** (70% yield), which was shown by MS and ^{1}H NMR measurements to be a tetramer of 3,3-dimethylbut-1-yne.[11] A single crystal X-ray crystallographic analysis[12] demonstrated that **2** was a linear tetramer, and this was confirmed spectroscopically as being a triene-yne (Scheme 1).



Scheme 1. Proposed pathway to the triene-yne **2**. [Rh] = [Rh(cod)]$^+$. a) CH_2Cl_2; b) THF; c) tBuC$_2$H; d) $-$ [Rh(cod)(thf)]$^+$.

Although there are recent reports of the formation of ene-ynes,[3] butatrienes,[4] and diene-ynes[5] from metal-promoted linear dimerization and trimerization reactions of alkynes, the regio- and stereoselective synthesis of **2** represents the first example of a linear tetramerization reaction, which is especially interesting because of its solvent dependency.

It is suggested that in the reaction between $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$, $AgPF_6$, and tBuC$_2$H in dichloromethane an η^2-alkyne complex **A** (Scheme 1) is formed, which selectively rearranges into the vinylidene species **B**, a clear precursor of the fulvene ligand.[6, 8] However, a different pathway is followed in THF, the η^2-alkyne complex **A** transforms into the hydridoacetylide–rhodium(III) complex **C**,[13] thus opening the way to the sequential "insertion"[14, 15] of tBuC$_2$H (**C** → **D** → **E** → **F**) and the formation, through reductive elimination, of the triene-yne **2**. Each of these steps is highly selective and although in principle both **D** and **E** could reductively eliminate to form an ene-yne or diene-yne, respectively, it is only when the third alkyne inserts (**E** → **F**) with different selectivity[14] to the two previous steps that reductive elimination intervenes and halts the oligomerization process.[16]

With this insight the way seemed to be clear to establish a catalytic procedure for the formation of the triene-yne **2**, and consequently a solution of $[Rh(NCMe)_2(cod)][BF_4]$ in THF was treated with 100 molar equivalents of tBuC$_2$H at 50 °C for 1 h. The color of the reaction mixture rapidly changed from yellow to red, but surprisingly on work up it was evident that only a relatively small amount of **2** had been formed. However, there was a new product present (60% yield), which was separated and purified by column chromatography (silica gel; hexane). The ^{1}H, ^{13}C NMR, and MS data[17] of this hydrocarbon-soluble material showed it to be a mononuclear rhodium complex **3** containing a cod ligand and an unusual organic ligand assembled from four tBuC$_2$H molecules. In this ligand one of the tBu groups has been transformed into a CH_2CMe_2 fragment, and loss of H^+ has occurred: consequently the product **3** is neutral. Attempts to establish the structural identity of **3** by X-ray crystallography were

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frustrated by the high solubility of the material. However treatment of **3** with $[FeCp_2][BF_4]$ (CH_2Cl_2, $-78\,^{\circ}C$) led to a 17e cationic species formed by a one electron oxidation reaction. Loss of $H^{\cdot}$ from this intermediate gave the diamagnetic cationic complex **4**. An X-ray diffraction study[18] of **4** following recrystallization (CH_2Cl_2/Et_2O) established the structure of the cation in this complex as that shown in Figure 1. Complex **4** contains two linked C_5 rings and is formed by a type of alkyne coupling reaction previously unobserved.

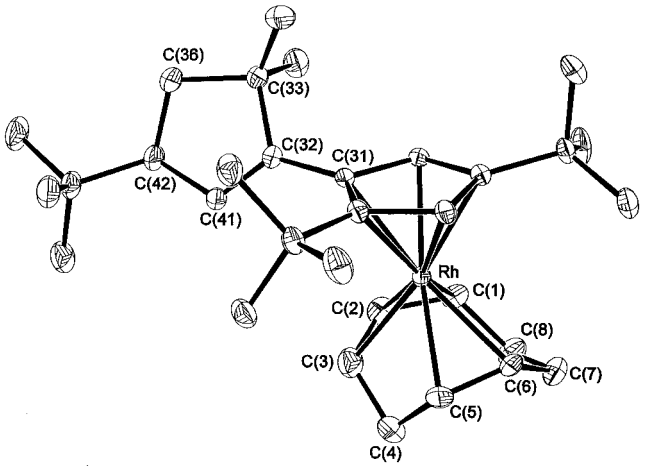
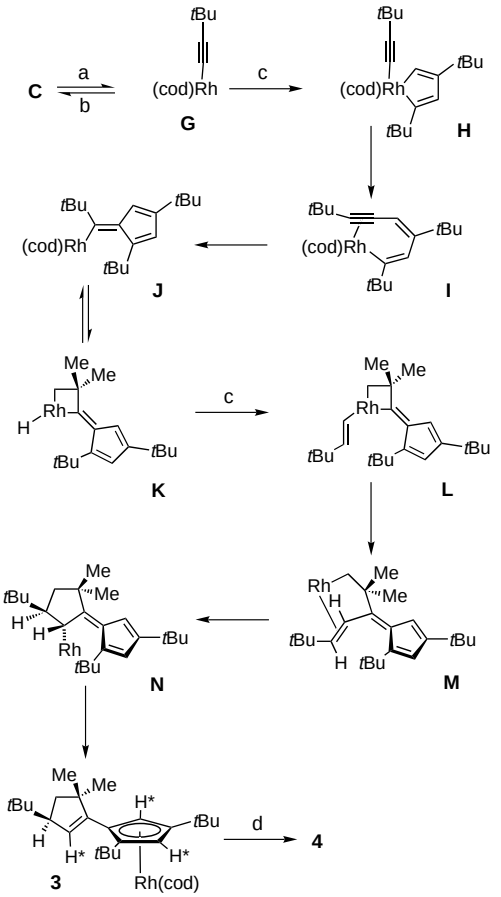


Figure 1. Solid-state structure of **4** (the hydrogen atoms and the BF_4^- counterion are removed for clarity). Selected bond lengths [Å]: Rh-C(1) 2.182(3), Rh-C(2) 2.143(3), Rh-C(3) 2.303(3), Rh-C(5) 2.228(3), Rh-C(6) 2.222(3), C(31)-C(32) 1.484(4), C(32)-C(41) 1.333(3), C(32)-C(33) 1.542(4), C(33)-C(36) 1.547(4), C(36)-C(42) 1.540(4), C(41)-C(42) 1.507(4).



Scheme 2. Proposed pathway to complex **3** in THF. a) $-H^+$; b) $+H^+$; c) tBuC$_2$H; d) $[FeCp_2]BF_4$; the cod ligands have been omitted for clarity in species **K**–**N**.

Comparison of the NMR data for **3** with that of the cation **4** clearly showed that the redox reaction involved only the cycloocta-1,5-diene ligand, which was transformed into an ene-η^3-allyl system.[19] Therefore, with the structural identity of **3** (Scheme 2) established it is reasonable to consider a possible reaction pathway to this novel product. In agreement with the pathway outlined in Scheme 1, the reaction in THF at low concentrations of tBuC$_2$D afforded the triene-yne **2**, in which only the vinylic CH bonds had been replaced by CD. However, at high tBuC$_2$D concentrations, when the catalytic reaction stops because of the formation of the neutral complex **3**, deuterium atoms are incorporated into the three asterisked positions of **3**, (Scheme 2), which suggests that a terminal alkyne hydrogen atom is lost.

The formation of **3** and the results from the deuterium labeling experiments can be rationalized if it is assumed that the hydridoacetylide **C** is reversibly deprotonated in the basic solvent THF to give the neutral complex **G** (Scheme 2), which is presumably stabilized by the coordination of THF. At high alkyne concentrations **G** can be captured by tBuC$_2$H resulting in the formation of the rhodiacyclopentadiene **H** and the diversion of the rhodium away from the triene-yne forming process. Once formed, **H** could be expected to undergo a reductive elimination reaction to form the alkyne complex **I**, thus providing access to the σ-bonded fulvene derivative **J**. As a result of the proximity of the α-tBu substituent to the rhodium center **J** would be expected to readily undergo a reversible C–H activation reaction leading, via the intermediates **L**, **M**, and **N**, to complex **3**.

There is no precedent for a reaction of this type, and it is especially interesting that the course of the reaction between a putative $[Rh(cod)]^+$ fragment and tBuC$_2$H is dependent in a subtle way on both the choice of the reaction solvent and on the alkyne concentration. We have also found in a preliminary study of the corresponding system in which the cod ligand is replaced by norbornadiene that although the triene-yne **2** is formed, there is no evidence for the formation of a norbornadiene-substituted analogue of **3**. This observation has interesting consequences for the development of a catalytic synthesis of the triene-yne.

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[11] **2**: ^{1}H NMR ($CDCl_3$): $\delta = 1.08$ (s, 9H; CMe_3), 1.10 (s, 9H; CMe_3), 1.12 (s, 9H; CMe_3), 1.32 (s, 9H; CMe_3), 5.61 (d, $^3J = 15.9$ Hz, 1H; CH), 5.85 (d, $^3J = 15.9$ Hz, 1H; CH), 6.57 (d, $^3J = 10.8$ Hz, 1H; CH), 6.62 (d, $^3J = 10.8$ Hz, 1H; CH); ^{13}C NMR ($CDCl_3$): $\delta = 28.3$ (CMe_3), 29.4 (CMe_3), 29.5 (CMe_3), 29.6 (CMe_3), 31.3 (CMe_3), 33.6 (CMe_3), 35.7 (CMe_3), 36.1 (CMe_3), 77.1 ($C{\equiv}C$), 106.4 ($C{\equiv}C$), 121.1 (=CH), 121.3 (=CH), 129.0 (=CH), 132.6 (=C*t*Bu), 147.6 (=CH), 151.1 (=C*t*Bu); EI-MS: *m*/*z*: 328.3 [M^+], 271.3 [$M^+ - CMe_3$], 215.2 [$M^+ - 2CMe_3$].

[12] Crystal structure analysis of **2**, $C_{24}H_{40}$: $M_r = 328.56$, monoclinic, space group $P2_1/c$, $a = 10.001(3)$, $b = 12.231(3)$, $c = 10.237(3)$ Å, $\beta = 113.55(2)^\circ$, $V = 1147.9(6)$ Å^3, $Z = 2$, $\mu = 0.052$ mm^{-1}, crystal dimensions $0.25 \times 0.25 \times 0.2$ mm. $2\theta_{max} = 50^\circ$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), $T = 170(2)$ K, 2181 measured reflections, of which 2016 were unique and 1058 observed with $F_o > 4\sigma(F_o)$. Lorentz and polarization corrections were applied and the structure solved by direct methods (SHELX86) with full-matrix least-squares (SHELXL93) refinement based on F^2. 115 parameters. $R1 = 0.1111$, $wR2 = 0.3159$.[20] The asymmetric unit consists of one half of the triene-yne with the remainder generated by an inversion center, hence there is disorder between the terminal double and triple bonds.

[13] It is also possible that the vinylidene complex **B** is formed via the hydridoacetylide complex **C**.

[14] A. M. La Pointe, M. Brookhart, *Organometallics* **1998**, *17*, 1530 – 1537. In this study of the reactions of alkynes with the cationic complexes $[Pd(CH_3)(N{-}N)L][BAr^1_4]$ (N–N = phenanthroline or diimine, L = Et_2O or MeCN, $Ar^1 = 3,5\text{-}(CF_3)_2C_6H_3$) the regiochemistry of the "insertion" step has been related to the steric demands of both the metal center and the alkyne. It is also reported in this paper that an excess of alkyne results in the formation of a palladium – trienyl species that can then undergo an intramolecular cyclization reaction to form a 5-ethylidene-2-cyclopentene-1-yl complex. Although a related intramolecular cyclization reaction with the rhodium – trienyl intermediate **F** (shown in Scheme 1) can be envisaged, such a process does not provide a pathway to the fulvene complex **1**.

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[16] In the case of the cobalt system studied by Klein and co-workers[5] a shut down of the oligomerization process is also observed on reversal of the regiochemistry of the insertion of a monosubstituted alkyne (PhC_2H). However, in contrast with the rhodium system this occurs earlier in the oligomerization process.

[17] The ^{1}H NMR data for **3** indicated the presence of three compounds in the approximate ratio 8:2:1. The fact that all three species possessed near-identical NMR spectra led us to conclude that they were all stereoisomers. In contrast, the ^{1}H NMR spectrum of the crystals of **4** showed evidence for the presence of only one stereoisomer. NMR data for the major steroisomer of **3**: ^{1}H NMR ($CDCl_3$): $\delta = 0.85$ (s, 9H; CMe_3), 0.89 (s, 3H; CMe_2), 1.01 (s, 3H; CMe_2), 1.19 (s, 9H; CMe_3), 1.21 (s, 9H; CMe_3), 1.45 (dd, $^2J = 11.7$, $^3J = 8.8$ Hz, 1H), 1.67 (dd, $^2J = 11.7$, $^3J = 6.3$ Hz, 1H), 1.73 (m, 2H; cod CH_2), 1.98 (m, 2H; cod CH_2), 2.08 (m, 2H; cod CH_2), 2.18 (m, 2H; cod CH_2), 2.54 (ddd, $^3J = 8.8$, $^3J = 6.3$, $^3J = 1.5$ Hz, 1H), 3.58 (m, 2H; cod CH), 3.83 (m, 2H; cod CH), 4.28 (d, $^4J = 2.4$ Hz, 1H; Cp), 4.50 (d, $^4J = 2.4$ Hz, 1H; Cp), 5.80 (d, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 27.2$ (s; CMe_2), 27.9 (s; CMe_3), 28.5 (s; CMe_2), 31.6 (s; cod CH_2), 32.3 (s; CMe_3), 33.4 (s; CMe_3), 33.5 (s; cod CH_2), 44.5 (s; CH_2), 47.4 (s; CMe_2), 53.8 (s; CH*t*Bu), 63.5 (d, $^1J_{RhC} = 14.4$ Hz; cod CH), 66.8 (d, $^1J_{RhC} = 14.4$ Hz; cod CH), 80.6 (d, $^1J_{RhC} = 3.3$ Hz; Cp CH), 81.9 (d, $^1J_{RhC} = 4.4$ Hz; Cp CH), 101.6 (d, $^1J_{RhC} = 4.4$ Hz; Cp CC), 116.1 (d, $^1J_{RhC} = 4.4$ Hz; Cp CC), 117.7 (d, $^1J_{RhC} = 3.3$ Hz; Cp CC), 133.8 (s; CH=C), 146.8 (s; CH=C); FAB MS of **3**: *m*/*z*: 538.2 [M^+], 481.1 [$M^+ - CMe_3$].

[18] Crystal structure analysis of **4**, $C_{32}H_{50}BF_4Rh$: $M_r = 624.44$, triclinic, space group $P\bar{1}$, $a = 8.931(2)$, $b = 9.389(2)$, $c = 20.404(9)$ Å, $\alpha = 103.12(3)$, $\beta = 90.14(3)$, $\gamma = 110.72(2)^\circ$ $V = 1552.1(8)$ Å^3, $Z = 2$, $\mu = 0.593$ mm^{-1}, crystal dimensions $0.40 \times 0.20 \times 0.05$ mm. $2\theta_{max} = 55^\circ$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 173(2)$ K, 16005 measured reflections, of which 7020 were unique ($R_{int} = 0.0332$) and observed. Full-matrix least-squares refinement based on F^2. 382 parameters.[20] $R1 = 0.0361$, $wR2 = 0.0807$. NMR data for **4**: ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (s, 9H; CMe_3), 1.05 (s, 3H; CMe_2), 1.26 (s, 3H; CMe_2),1.33 (s, 9H; CMe_3), 1.34 (s, 9H; CMe_3), 1.59 (dd, $^2J = 11.8$, $^3J = 10.8$ Hz, 1H), 1.80 (dd, $^2J = 11.8$, $^3J = 6.5$ Hz, 1H), 2.29 (m), 2.55 (m), 2.74 (dd, $^3J = 10.8$, $^3J = 6.5$ Hz, 1H), 2.88 (m), 3.32 (m), 3.83 (m), 4.59 (m), 4.71 (m), 5.04 (m), 5.23 (d, $^4J = 1.7$ Hz, 1H; Cp), 5.46 (d, $^4J = 1.7$ Hz, 1H; Cp), 5.85 (m), 6.01 (d, $^3J < 1$ Hz, 1H).

[19] A similar reaction has been observed on treatment of [Rh(cod)Cp] with one-electron oxidants: M. D. Kitchen, PhD thesis, University of Bristol (UK), **1978**; N. G. Connelly, personal communication.

[20] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-118903 (**2**) and -118904 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

An Atmospherically Driven Optical Switch

James J. La Clair*

An effective switch translates an external force through components of minimal complexity into a signal that regulates a desired output. A series of macromolecular switches have now been constructed that can be initiated by chemical, electrochemical, photochemical, or thermal stimuli.[1] Recent attention now focuses on adapting these materials into machines or electronic components.[2] A new device is presented that translates a change in the atmosphere into an electrical output though a photophysical change within a small group of molecules.

Here, a change is defined in units of molecules and measured by monitoring the viability of twisted intramolec-

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