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A Highly Efficient Route to Ferrocene Derivatives Containing Four-Carbon Heteroannular Bridges via a Novel Cyclization Reaction

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Summary: **Synthesis of 1,1′-bis((trimethylsilyl)ethynyl)ferrocene and conversion of this compound to a ferrocene derivative containing a 1-methoxy-1,3-butadienyl heteroannular bridging unit via a novel, catalytic, and high-yielding cyclization reaction are described. Simple synthetic transformations of this reactive bridging unit readily yield ferrocene derivatives containing four-carbon heteroannular bridges.**

A large number of ferrocene derivatives containing heteroannular bridges have been reported.[1] Ferrocene derivatives containing α-ketotrimethylene heteroannular bridges[1a–c] are prepared via acid-catalyzed cyclization reactions of β-ferrocenyl carboxylic acids.[1a,2] If γ-ferrocenyl acids are employed in these reactions, the result is homoannular rather than heteroannular cyclized products.[1a] Ferrocenes containing four-carbon heteroannular bridges are frequently prepared from the corresponding α-ketotrimethylene-bridged derivative via ring expansion with diazomethane.[1c] We report herein a new entry to ferrocene derivatives containing four-carbon heteroannular bridges via the highly efficient conversion of 1,1′-diiodoferrocene[3] in two steps to a ferrocene derivative in which the cyclopentadienyl rings are bridged by a 1-methoxy-1,3-butadienyl unit. This conversion involves a novel and catalytic cyclization reaction between alkynyl groups on the opposing cyclopentadienyl rings of 1,1′-diethynylferrocene. We report here our studies of the cyclization reaction pathway and describe synthetic transformations of this bridging unit.

As part of our studies directed toward the incorporation of transition metals into glassy-carbon materials,[4] we attempted the preparation of the diacetylenic iron-containing monomer 1,1′-diethynylferrocene (4). Our intended route to this monomer involved the coupling reaction[5] of 1,1′-diiodoferrocene[3] (1) with 2 equiv of (trimethylsilyl)acetylene catalyzed by 4 mol % of $(Ph_3P)_2PdCl_2$ and $Cu(OAc)_2 \cdot H_2O$ in refluxing diisopropylamine, which gave 1,1′-bis((trimethylsilyl)ethynyl)ferrocene (**2**) in 80% isolated yield (Scheme I).[6] On treatment of **2** with a catalytic quantity of aqueous potassium hydroxide in methanol at room temperature[7] we were surprised to discover that, rather than the expected diethynyl derivative **4**, the *only* product isolated from this reaction was the bridged ferrocene derivative **5**, which was recovered in 85% yield by flash chromatographic separation over silica gel with 1.5% (v/v) triethylamine in hexane as the eluant.[8,9]

A possible reaction pathway for the formation of **5** is illustrated in Scheme I. Sequential desilylation[7] of **2** initially generates 1-ethynyl-1′-((trimethylsilyl)ethynyl)ferrocene (**3**) followed by formation of **4**. This latter compound suffers methoxide attack at an sp carbon center α to the cyclopentadienyl ring followed by intramolecular cyclization onto the β-carbon of the adjacent alkynyl group.[10,11] Proton abstraction from methanol gives the four-carbon heteroannular bridged vinyl ether ferrocene derivative **5** and regenerates methoxide ion.

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(1) For example, see: (a) Rinehart, K. L.; Curby, R. J.; Gustafson, D. H.; Harrison, K. G.; Bozak, R. E.; Bublitz, D. E. *J. Am. Chem. Soc.* **1962**, *84*, 3263. (b) Rinehart, K. L.; Curby, R. J. *J. Am. Chem. Soc.* **1957**, *79*, 3290. (c) Rosenblum, M.; Banerjee, A. K.; Danieli, N.; Fish, R. W.; Schlatter, V. *J. Am. Chem. Soc.* **1963**, *85*, 316. (d) Lentzner, H. L.; Watta, W. E. *Tetrahedron* **1971**, *27*, 4343. (e) Yasufuku, K.; Yamazaki, H. *J. Organomet. Chem.* **1977**, *127*, 197. (f) Salisova, M.; Toma, S.; Solcaniova, E. *J. Organomet. Chem.* **1977**, *132*, 419. (g) Sonoda, A.; Moritani, I. *J. Organomet. Chem.* **1971**, *26*, 133. (h) Katz, T. J.; Acton, N.; Martin, G. *J. Am. Chem. Soc.* **1973**, *95*, 2934. (i) Hisatome, M.; Minagawa, S.; Yamakawa, K. *J. Organomet. Chem.* **1973**, *55*, C82. (j) Hisatome, M.; Namiki, T.; Yamakawa, K. *J. Organomet. Chem.* **1976**, *117*, C23. (k) Barr, T. H.; Watts, W. E. *Tetrahedron* **1968**, *24*, 3219. (l) Hisatome, M.; Hillman, M. *J. Organomet. Chem.* **1981**, *212*, 217. (m) Nesmeyanov, A. N.; Rybinskaya, M. I.; Shul'pin, G. B.; Pogregnyak, A. A. *J. Organomet. Chem.* **1975**, *92*, 341. (n) Kasahara, A.; Izumi, T.; Shimizu, I. *Chem. Lett.* **1979**, 1119. (o) Hisatome, M.; Watanabe, J.; Yamakawa, K.; Iitaka, Y. *J. Am. Chem. Soc.* **1986**, *108*, 1333.

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(4) (a) Callstrom, M. R.; Neenan, T. X.; McCreery, R. L.; Alsmeyer, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 4954. (b) Pocard, N. L.; Alsmeyer, D. C.; McCreery, R. L.; Neenan, T. X.; Callstrom, M. R. *J. Am. Chem. Soc.* **1992**, *114*, 769.

(5) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. (b) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280. (c) Takahashi, S.; Kuromaya, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

(6) Spectral data for **2**: mp 60–68 °C; IR (KBr) 3113, 3097, 2956, 2896, 2151, 1455, 1407, 1249, 1042, 1034, 931, 842, 758, 728, 697 cm^{-1}; ^1H NMR (200.1 MHz, $CDCl_3$) δ 4.41 (t, *J* = 2 Hz, 4 H), 4.21 (t, *J* = 2 Hz, 4 H), 0.22 (s, 8 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 103.4, 91.2, 73.7, 71.5, 65.9, 0.21. Anal. Calcd for $C_{20}H_{26}FeSi_2$: C, 63.48; H, 6.93. Found: C, 63.18; H, 7.05.

(7) (a) Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1965**, *4*, 217. (b) Eaborn, C.; Eastmond, R.; Walton, D. R. M. *J. Chem. Soc. B* **1971**, 127.

(8) A typical procedure for the conversion of **2** to **5** is as follows. A deoxygenated solution of 0.22 g (0.58 mmol) of **2** in 25 mL of methanol was treated with 0.05 mL (0.1 mmol) of a 2.5 M solution of aqueous potassium hydroxide. The resulting mixture was stirred at 22 °C for 24 h and then added to 50 mL of water. This mixture was extracted with dichloromethane (2 × 30 mL), and the combined organic extracts were washed with brine (60 mL) and then dried over $MgSO_4$ and filtered. Removal of solvent in vacuo gave an orange residue, which was flash-chromatographed over 20 g of silica gel using 1.5% (v/v) triethylamine in hexane as eluant. An orange band eluted which, upon removal of solvent in vacuo, afforded 0.128 g (85%) of **5** as a viscous, orange oil: IR (neat) 3091, 3002, 2952, 2904, 2900, 2828, 1672, 1622, 1478, 1462, 1384, 1346, 1231, 1206, 1141, 1036, 1025, 985, 840, 806, 743 cm^{-1}; ^1H NMR (250.1 MHz, $CDCl_3$) δ 6.04 (d, *J* = 12.4 Hz, 1 H), 5.66 (dd, *J* = 12.4, 7.2 Hz, 1 H), 4.76 (d, *J* = 7.2 Hz, 1 H), 4.50 (t, *J* = 1.8 Hz, 2 H), 4.40 (t, *J* = 1.8 Hz, 2 H), 4.22 (t, *J* = 1.8 Hz, 2 H), 4.18 (t, *J* = 1.8 Hz, 2 H), 3.60 (s, 3 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 158.9, 126.4, 124.6, 97.4, 80.1, 77.0, 70.1, 69.9, 67.6, 67.4, 54.8; HRMS calcd for $C_{15}H_{14}FeO$ 266.0394, found 266.0402. The last traces of solvent could not be removed from **5**, and consequently elemental analysis proved unsatisfactory.

(9) Additionally, we have prepared ((trimethylsilyl)ethynyl)ferrocene in 85% isolated yield via the coupling reaction between iodoferrocene and (trimethylsilyl)acetylene catalyzed by 5 mol % of $(Ph_3P)_2PdCl_2$ and $Cu(OAc)_2 \cdot H_2O$ in refluxing diisopropylamine. Spectral data for ((trimethylsilyl)ethynyl)ferrocene: mp 53.5–54.5 °C; IR (KBr) 3101, 3090, 2956, 2897, 2148, 1452, 1411, 1250, 1104, 1025, 1000, 925, 858, 810, 758, 726 cm^{-1}; ^1H NMR (200.1 MHz, C_6D_6) δ 4.40 (t, *J* = 2 Hz, 2 H), 4.03 (s, 5 H), 3.83 (t, *J* = 2 Hz, 2 H), 0.24 (s, 9 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 104.2, 90.5, 71.7, 70.1, 68.7, 64.9, 0.25. Anal. Calcd for $C_{15}H_{18}FeSi$: C, 63.83; H, 6.43. Found: C, 64.06; H, 6.47. In contrast to the result obtained with **2**, treatment of this compound with a catalytic quantity of aqueous potassium hydroxide in methanol at room temperature resulted in conversion to ethynylferrocene in 97% isolated yield. No products resulting from methoxide attack on the ethynyl group were detected.

(10) For examples of nucleophilic attacks on acetylenes, see: Dickstein, J. I.; Miller, S. I. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978; Part 2, pp 813–955.

(11) The regiochemistry of the methoxide attack can perhaps be explained by the high stabilizing ability of α-ferrocenyl groups on vinyl carbocations. For a discussion of the ability of ferrocenyl substituents to stabilize carbocations, see: Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985; Chapter 9.

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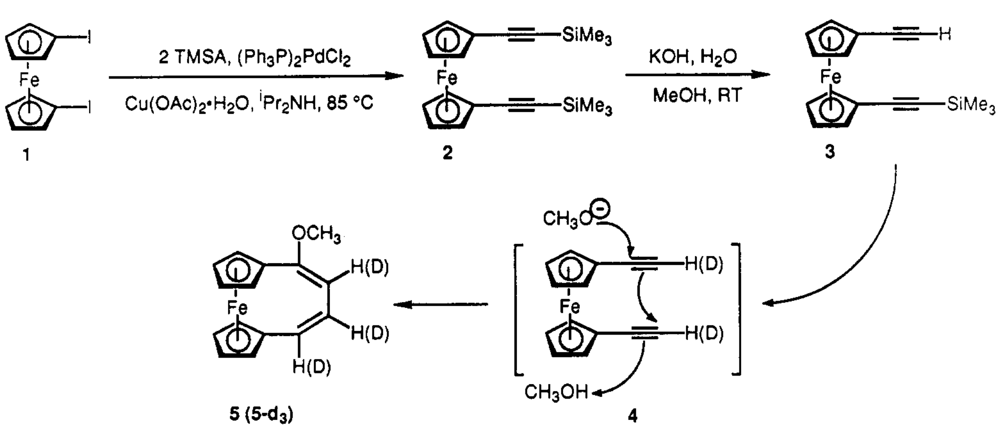
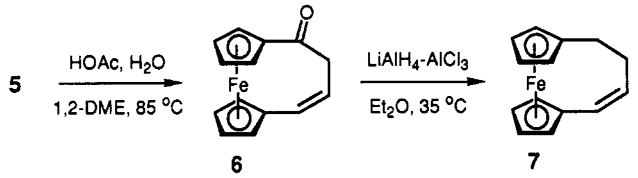
Scheme I



In an effort to determine if **3** and/or **4** were intermediates in the reaction, we carefully monitored the desilylation reaction of **2** by gas chromatographic (GC) analysis, which revealed the formation of an intermediate that appeared immediately after addition of potassium hydroxide but disappeared upon completion of the reaction. When the desilylation reaction was monitored by GC analysis with mass spectrometry detection, we found that the parent ion of the intermediate species (*m/e* 306) corresponded to that expected for **3**. In an effort to isolate this intermediate, a desilylation reaction was quenched at the maximum formation of this species and an orange oil, containing only an inseparable mixture of **2** and the intermediate by GC analysis, was obtained by chromatographic separation over silica gel. Spectral analysis of this mixture is consistent with that expected for **3** along with **2**. ^{1}H NMR spectroscopic analysis found triplets with chemical shifts of 4.44 and 4.23 ppm and a singlet with a chemical shift of 2.76 ppm. The former resonances are assigned to the α- and β-protons of the ethynyl-substituted cyclopentadienyl ring of **3**, while the latter resonance is assigned to the acetylenic proton.[12] The infrared spectrum of the mixture includes a strong band at 3308 cm^{-1}, which is assigned to the acetylenic CH stretch in **3**. We were unable to detect **4**, suggesting that this species cyclizes rapidly upon its formation, although the intermediacy of a trimethylsilyl-substituted bridged species cannot be ruled out.

The reaction pathway in Scheme I requires that all three of the vinyl protons in the bridge of **5** originate from the solvent. In order to test this requirement, a solution of **2** in CH_3OD at room temperature was treated with a catalytic quantity of potassium hydroxide introduced in D_2O. High-resolution mass spectral analysis found that three deuterium atoms had been incorporated into the resulting product, **5**-d_3, which was recovered in 85% yield.[13] The ^{1}H NMR spectrum of **5**-d_3 exhibited the expected resonances for the cyclopentadienyl and methoxy protons, but the resonances of the vinyl bridge protons were absent, indicating that deuterium had been incorporated at these positions. Analysis of the proton-decoupled ^{13}C NMR spectrum of **5**-d_3 found the resonances for the three vinyl bridge carbons to be split into the expected triplets.

Scheme II



We have probed the reactivity of the heteroannular bridge formed in **5** and have found that the vinyl ether group is extremely labile to hydrolysis. Only upon addition of 1–2% (v/v) of triethylamine to the eluant during chromatographic purification over silica gel could **5** be obtained without significant hydrolysis of this group. Treatment of **5** with aqueous acetic acid in refluxing 1,2-dimethoxyethane gave **6**, as the only detectable product, in 76% recovered yield (Scheme II).[14] All of the available spectral evidence indicates that the bridge olefin in **6** remains in the β,γ-position relative to the carbonyl group. We found that the carbonyl group in **6** could be directly reduced to the corresponding methylene group via treatment with $LiAlH_4$–$AlCl_3$[1d,15] in refluxing ether, giving **7** in 83% yield.[16] While the reduction product derived from the α,β-unsaturated ketone would afford 5 resonances in its proton-decoupled ^{13}C NMR spectrum, the ^{13}C NMR spectrum of **7** contained 10 resonances, clearly indicating the asymmetry of this compound with respect to the location of the bridge olefin. While it may be surprising that the bridge olefin in **6** does not isomerize into conjugation with the carbonyl group under the acidic hydrolysis conditions employed for its preparation from the vinyl ether precursor, analysis of molecular models reveals the α,β-isomer to be much more strained than the β,γ-isomer.

In summary, we have discovered a novel heteroannular cyclization reaction of 1,1′-bis((trimethylsilyl)ethynyl)ferrocene. The bridging unit generated in this reaction is

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(12) The acetylenic proton of ethynylferrocene has a chemical shift of 2.72 ppm in $CDCl_3$. For a preparation of ethynylferrocene, see: Rosenblum, M.; Brawn, N.; Papenmeier, J.; Applebaum, M. *J. Organomet. Chem.* **1966**, *6*, 173.

(13) Spectral data for **5**-d_3: IR (neat) 3092, 2995, 2951, 2932, 2903, 2827, 2237, 1614, 1463, 1376, 1293, 1257, 1202, 1147, 1067, 1025, 986, 854, 838, 806 cm^{-1}; ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 4.49 (t, J = 2 Hz, 2 H), 4.39 (t, J = 2 Hz, 2 H), 4.21 (t, J = 2 Hz, 2 H), 4.17 (t, J = 2 Hz, 2 H), 3.59 (s, 3 H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 159.6, 126.4 (t, J = 23 Hz), 124.5 (t, J = 24 Hz), 97.2 (distorted triplet, J = 22 Hz), 80.3, 77.6, 70.4, 70.3, 68.2, 67.8, 54.4; HRMS calcd for $C_{15}H_{11}D_3FeO$ 269.0582, found 269.0579.

(14) Spectral data for **6**: mp 124–125 °C; IR (KBr) 3110, 3100, 3018, 2955, 2930, 1652, 1636, 1448, 1373, 1290, 1264, 1079, 1039, 1032, 890, 831, 820, 716 cm^{-1}; ^{1}H NMR (200.1 MHz, C_6D_6) δ 6.03 (dt, J = 10.9, 7.1 Hz, 1 H), 5.77 (dt, J = 10.9, 1.5 Hz, 1 H), 4.37 (t, J = 2 Hz, 2 H), 4.04 (t, J = 2 Hz, 2 H), 3.83 (t, J = 2 Hz, 2 H), 3.74 (t, J = 2 Hz, 2 H), 2.99 (dd, J = 7.1, 1.5 Hz, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 202.5, 132.5, 123.7, 89.5, 79.1, 74.3, 70.5, 70.0, 69.4, 39.0. Anal. Calcd for $C_{14}H_{12}FeO$: C, 66.70; H, 4.80. Found: C, 67.05, H, 4.94.

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(16) Spectral data for **7**: mp 58–60 °C; IR (KBr) 3077, 3008, 2934, 2908, 2862, 2844, 1645, 1444, 1394, 1322, 1228, 1206, 1040, 1027, 851, 810, 746, 719, 521, 489, 474 cm^{-1}; ^{1}H NMR (250.1 MHz, C_6D_6) δ 6.20 (d, J = 11.3 Hz, 1 H), 5.75 (dt, J = 11.3, 8.3 Hz, 1 H), 4.03–3.99 (m, 6 H), 3.76 (t, J = 1.8 Hz, 2 H), 2.24–2.17 (m, 2 H), 1.76–1.72 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 131.5, 125.5, 85.3, 80.6, 69.8, 69.3, 68.5, 68.4, 27.7, 21.2. Anal. Calcd for $C_{14}H_{14}Fe$: C, 70.62; H, 5.93. Found: C, 70.70; H, 5.92.

readily transformed, allowing for the preparation of additional ferrocene derivatives containing four-carbon heteroannular bridges. Further studies of this novel cyclization reaction of 1,1′-bis((trimethyl)ethynyl)ferrocene and similar systems are currently in progress.

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Synthesis and X-ray Characterization of the Neutral Organometallic Gold Cluster $[Au_{10}(C_6F_5)_4(PPh_3)_5]$

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Summary: The reaction of $[Au_9(PPh_3)_8](NO_3)_3$ with 3 equiv of $NBu_4[Au(C_6F_5)_2]$ affords the neutral cluster $[Au_{10}(C_6F_5)_4(PPh_3)_5]$ in high yield. X-ray diffraction reveals that the cluster has a toroidal geometry based on a ring of edge- and face-sharing tetrahedra that share a common central vertex. It crystallizes in space group $P2_1/c$ with a = 18.339 (4) Å, b = 15.603 (4) Å, c = 41.510 (12) Å, β = 95.10 (2)°, and Z = 4. This cluster represents the second example of both an Au_{10} and an organometallic gold cluster.

Gold forms a wide range of cluster compounds in which the metal has an oxidation state between 0 and +1. These compounds are generally stabilized by tertiary phosphine ligands,[1,2] in contrast to many high-nuclearity metal clusters that have CO as ligands.[2,3]

Many examples of gold clusters are known from Au_3 to Au_{13} with a variety of geometries and have been classified by Mingos and Hall[2] as (a) spherical polyhedral clusters characterized by a total of $12n + 18$ valence electrons (n is the number of peripheral gold atoms), e.g. $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$,[4] and (b) toroidal or elliptical polyhedral clusters characterized by a total of $12n + 16$ valence electrons, e.g. $[Au_9\{P(p\text{-tol})_3\}_8]^{3+}$.[5]

The lack of organometallic gold clusters in this field is noteworthy; only one example has been reported, namely $[Au_5(dppmH)_3(dppm)](NO_3)_2$,[6,7] where one deprotonated dppm ligand forms an Au–C bond. Similarly, Au_{10} derivatives are very poorly represented; only the cluster $[Au_{10}Cl_3(PCy_2Ph)_6](NO_3)$[8] has been synthesized in low yield.

Here we report the synthesis and characterization by elemental analysis, IR and NMR spectroscopy, fast atom bombardment mass spectrometry, and single-crystal X-ray diffraction of $[Au_{10}(C_6F_5)_4(PPh_3)_5]$.

The reaction of $[Au_9(PPh_3)_8](NO_3)_3$ with $NBu_4[Au(C_6F_5)_2]$ (molar ratio 1:3) in dichloromethane yielded, after separation of NBu_4NO_3, the orange solid $[Au_{10}(C_6F_5)_4(PPh_3)_5]$ (80% yield).[9] The fact that no other cluster species has been detected and that $[Au(C_6F_5)PPh_3]$ is also formed led us to propose the reaction

$$[Au_9(PPh_3)_8](NO_3)_3 + 3NBu_4[Au(C_6F_5)_2] \rightarrow [Au_{10}(C_6F_5)_4(PPh_3)_5] + 3NBu_4NO_3 + 2[Au(C_6F_5)PPh_3] + PPh_3$$

The IR spectrum of $[Au_{10}(C_6F_5)_4(PPh_3)_5]$ exhibits bands due to the C_6F_5 group[10,11] at 1496 (s), 1068 (s, br), 951 (s), and 782 (s) cm^{-1}; the last band is very sensitive to the nature of the ligand in the trans position and to the oxidation state and therefore appears for $[Au(C_6F_5)_2]^-$ at 780 cm^{-1} and for $[Au(C_6F_5)L]$ complexes in the range 790–800 cm^{-1}. In our complex this band is found between these two values.

The mass spectrum (over m/z 2000) gave the most abundant mass ion at m/z 3782, which corresponds not

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[8] Briant, C. E.; Hall, K. P.; Wheeler, A. C.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1984**, 248.

[9] Procedure: To a dichloromethane solution (30 mL) of $[Au_9(PPh_3)_8](NO_3)_3$ (0.405 g, 0.1 mmol) was added $NBu_4[Au(C_6F_5)_2]$ (0.232 g, 0.3 mmol). After 3 h the solvent was evaporated to dryness and 30 mL of diethyl ether added. The white solid (NBu_4NO_3) was filtered off and the solution evaporated to ca. 10 mL. Addition of n-hexane gave $[Au_{10}(C_6F_5)_4(PPh_3)_5]$ (80%). Anal. Calcd: C, 34.67; H, 1.91. Found: C, 34.67; H, 1.86. Λ_M = 5 Ω^{-1} cm^2 mol^{-1} in acetone. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 58.5 (s, br) ppm; −60° C, δ 64.4 (br), 53.3 (br), 49.4 (br) ppm. ^{19}F NMR ($CDCl_3$): δ −112.51 (m, 4 F, o-F) −162.79 [t, 2 F, p-F, J(FF) = 20.8 Hz], −163.36 (m, 4 F, m-F).

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