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Synthesis, Characterization, and Structural Studies of Transition Metal Open Fulvalene Complexes

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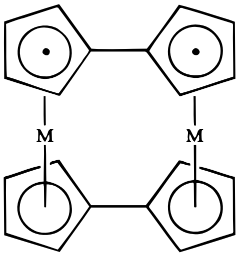
Starting from the 3-methylpentadienyl anion, a route to 3,8-dimethyl-1,3,5,7,9-decapentaene has been devised. This pentaene reacts readily with $Co(C_5H_5)(C_2H_4)_2$ or $[Ru(C_5Me_5)Cl]_4$ (2 and 0.5 equiv, respectively) to yield the expected ($\eta^4,\eta^{4'}$-decapentaene)dimetal complexes, in which the two external diene fragments of the pentaene are each coordinated to a metal center, leaving the central C═C bond uncoordinated. Subsequent respective two-electron oxidation or reduction then leads to ($\eta^5,\eta^{5'}$-dimethyldecapentaene)ML_n species (ML_n = $Co(C_5H_5)^+$ or $Ru(C_5Me_5)$). The first three complexes have been found to exist as mixtures of two isomers, and structural studies have confirmed the natures of the two open fulvalene ($\eta^5,\eta^{5'}$) complexes. A related reaction, involving the reduction of $[V(C_5H_5)Cl(PMe_3)_2]_2$ and the pentaene with magnesium, has been found to lead to a similar $\eta^5,\eta^{5'}$ complex for which ML_n = $V(C_5H_5)(PMe_3)$. Its structural nature has also been confirmed through a diffraction study.

A tremendous amount of effort has been, and is currently, devoted to the study of electronic communication and magnetic interactions in di- and polymetallic species.[1] For such organometallic complexes, particular attention has been devoted to compounds in which two metal centers are coordinated by a single fulvalene ligand.[2] Notably, some mixed valence bis(fulvalene)dimetal complexes (**1**), such as the known $M_2 = Fe_2^{5+}$ species, possess nearly, if not fully, delocalized ground states, such that the metal centers appear virtually equivalent.[3] In contrast, the extent of delocalization in related mono(fulvalene)dimetal species (**2**) generally tends to be significantly less, although subject to significant variation in response to sometimes subtle changes in external influences. It would therefore seem of interest to replace the cyclopentadienyl rings in **1** and **2** by open pentadienyl groups, which provide for much greater metal−ligand orbital mixing and could thereby lead to increased through-bond metal−metal interactions.[4] However, there are several ways in which an "open fulvalene" unit could be constructed, as the connection could be made through the 1, 2, or 3 position of the dienyl group, leading to significantly greater variety relative to fulvalene itself. In this regard, the end−end (**3**) and center−center (**4**) coupled possibilities should be of greatest interest, as only the end and center positions can formally bear radical or charge character.[5] Herein we report our initial efforts to expand upon the number of potentially bridging ligands available for organometallic chemistry through the preparation and



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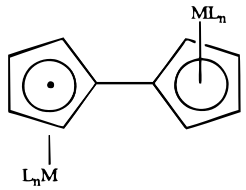

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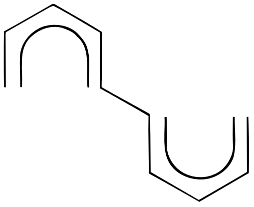
(5) Obviously one could envision also end−center-coupled open fulvalene ligands, which although being more complicated spectroscopically should lead to some interesting behavior as a result of the metal centers then becoming nonequivalent.

S0276-7333(98)00426-9 CCC: $15.00



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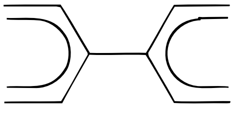

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characterization of transition metal complexes of open fulvalene ligands.

Experimental Section

All compounds were prepared and handled under a nitrogen atmosphere, either in a glovebox or using Schlenk techniques. Hydrocarbon and ethereal solvents were distilled from sodium/benzophenone ketyl under a nitrogen atmosphere, while methylene chloride was dried by distillation from P_4O_{10} under nitrogen, and nitromethane was dried for at least several days with molecular sieves prior to distillation under a nitrogen atmosphere. $Co(C_5H_5)(C_2H_4)_2$, $[Ru(C_5Me_5)Cl]_4$, and $V(C_5H_5)(Cl)_2(PMe_3)_2$ were prepared according to published procedures,[6] except that in the preparation of $V(C_5H_5)(Cl)_2(PMe_3)_2$, NaC_5H_5 was utilized instead of the magnesium reagent,[7] and a 60:40 hexane/THF solvent mixture was used for extraction and crystallization. ESR spectra were obtained on samples having concentrations of ca. $10^{-4}-10^{-5}$ M using an IBM-Bruker ESR spectrometer in the X-band frequency range. The modulation frequency was 100 kHz, and diphenylpicrylhydrazyl was used as an external standard ($g = 2.0038 \pm 0.0002$). Proton NMR assignments were confirmed through selective decoupling experiments. Other spectroscopic data were obtained as previously described.[8] Elemental analyses were obtained from Desert Analytics, Oneida Research Labs, or Mikroanalytische Laboratorium (Germany).

3,8-Dimethyl-1,3,7,9-decatetraene, 3,8-$(CH_3)_2(C_{10}H_{12})$. The compound 3,8-$(CH_3)_2(C_{10}H_{12})$ may be prepared in a manner analogous to the preparation of 2,4,7,9-tetramethyl-1,3,7,9-decatetraene.[9a] Thus, a solution of potassium 3-methylpentadienide, $K(3\text{-}C_6H_9)$[10] (3.6 g, 30 mmol), in 50 mL of THF was added dropwise to a stirred slurry of CuCl (3.6 g, 36 mmol) in 100 mL of THF at −78 °C. The mixture was allowed to warm slowly to room temperature and was then stirred for an additional 4 h, resulting in a black slurry. The solvent was removed in vacuo, and the product was extracted with two 50 mL portions of hexane. Filtration of the combined extracts through a Celite pad gave a clear, colorless solution. Upon total removal of the solvent, 2.0 g (12 mmol) of product, $C_{12}H_{18}$, was isolated as a colorless analytically and spectroscopically pure oil, corresponding to a yield of 81% based on $K(3\text{-}C_6H_9)$. The oil could be vacuum transferred at 60 °C onto a coldfinger (−78 °C), on which it solidified and subsequently remelted on warming to room temperature. Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.80; H, 11.11. ^1H NMR (chloroform-d_1, ambient): δ 6.36 (d of d, $J = 17.4$, 10.9 Hz, 2H, H-2), 5.48 (br, 2H, H-4), 5.08 (d, $J = 17.4$ Hz, 2H, H-1_{trans}), 4.93 (d, $J = 11.1$ Hz, 2H, H-1_{cis}), 2.22 (d, $J = 3.3$ Hz, 4H, H-5), 1.73 (s, 6H, CH_3). ^{13}C NMR (chloroform-d_1, ambient): δ 141.5 (d, $J = 149$ Hz, C-2 or 4), 134.5 (s, C-3), 132.3 (d, $J = 149$ Hz, C-2 or 4), 110.7 (t, $J = 155$ Hz, C-1), 28.2 (t, $J = 129$ Hz, C-5), 11.7 (q, $J = 128$ Hz, CH_3). Mass spectrum (EI, 17 eV) *m/z* (relative intensity): 163 (1), 162 (1), 95 (18), 93 (18), 83 (24), 82 (13), 81 (100), 79 (23), 69 (17), 67 (16), 55 (32), 53 (18). IR (neat): 3095 (s), 3040 (m), 3010 (s), 2982 (s, sh), 2940 (s, br), 2860 (s), 2832 (m, sh), 1788 (w), 1642 (m), 1608 (s), 1440 (m), 1413 (m), 1389 (m), 1362 (m), 1316 (w), 1294 (w), 1258 (w), 1079 (m), 989 (s), 915 (m, sh), 892 (s), 861 (m), 805 (w), 730 (w), 695 (w) cm^{-1}.

The Potassium Salt of the 3,8-Dimethyldecapentaene Dianion, $K_2[3,8\text{-}(CH_3)_2(C_{10}H_{10})]$. This compound may be synthesized in a method similar to that used for a bridged bis(pentadienyl) dianion.[9a] To a flask containing 2.50 g (25.2 mmol) of potassium *tert*-butoxide and 30 mL of hexane was added 11.0 mL (27.5 mmol) of a 2.5 M butyllithium solution at a temperature below −30 °C. After this mixture was warmed to room temperature, a solution of 1.96 g (12.0 mmol) of 3,8-$(CH_3)_2(C_{10}H_{12})$ in 20 mL of hexane was added. The reaction mixture was allowed to stir at room temperature for 3 h, during which time the potassium salt of the conjugated di(pentadienyl) dianion precipitated as a dark red powder. The product was collected on a frit and washed with two 20 mL portions of benzene, followed by two 20 mL portions of pentane. Upon drying in vacuo, 2.74 g (11.5 mmol) of the title compound, $K_2[3,8\text{-}(CH_3)_2(C_{10}H_{10})]$, was obtained, corresponding to a yield of 95% based on the decatetraene.

3,8-Dimethyl-1,3,5,7,9-decapentaene, [3,8-$(CH_3)_2(C_{10}H_{10})$]. White crystalline $ZnCl_2$ (1.1 g, 7.6 mmol) was suspended in 80 mL of THF in a 250 mL, three-neck flask equipped with a nitrogen inlet and a magnetic stirring bar. After this mixture was cooled to −78 °C, 1.5 g (6.5 mmol) of $K_2[3,8\text{-}(CH_3)_2(C_{10}H_{10})]$ was added to the stirred suspension via a solid addition funnel. The resulting orange-yellow solution was slowly warmed to room temperature, during which time it turned to a dark gray slurry. This dark gray slurry was then stirred for an additional 3 h. The solvent was removed in vacuo after the reaction was complete, and the product was extracted with two 40 mL portions of hexane. The combined extracts were filtered through a Celite pad, yielding a bright yellow solution. After total removal of the solvent, the decapentaene ($C_{12}H_{16}$, 0.19 g, 1.2 mmol) was sublimed under vacuum at 55−60 °C from the residue, yielding a white solid (mp 88−89 °C). The yield was 19% based on $K_2[3,8\text{-}(CH_3)_2(C_{10}H_{10})]$. Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.90; H, 10.18. ^1H NMR (chloroform-d_1, ambient): δ 6.61 (d of d, $J = 7.8$, 3.0 Hz, 2H, H-4 or 5), 6.44 (d of d, $J = 17.1$, 10.5 Hz, 2H, H-2), 6.20 (d of d, $J = 7.8$, 3.0 Hz, 2H, H-4 or 5), 5.23 (d, $J = 17.1$ Hz, 2H, H-1_{trans}), 5.06 (d, $J = 10.5$ Hz, 2H, H-1_{cis}), 1.89 (s, 6H, CH_3). ^{13}C NMR (chloroform-d_1, ambient): δ 141.2 (d, $J = 153$ Hz, C-2,4 or 5), 136.0 (s, C-3), 132.0 (d, $J = 151$ Hz, C-2,4 or 5), 129.9 (d, $J = 151$ Hz, C-2,4 or 5), 112.8 (t, $J = 157$ Hz, C-1), 12.1 (q, $J = 127$ Hz, CH_3). Mass spectrum (EI, 17 eV) *m/z* (relative intensity): 160 (100), 145 (80), 131 (10), 130 (14), 129 (11), 117 (13), 105 (50), 92 (45), 91 (64), 81 (17), 80 (69), 79 (17), 77 (15), 53 (14). IR (Nujol mull): 3084 (w), 3028 (m, sh), 1790 (w), 1608 (m, sh), 1599 (m), 1568 (w), 1412 (w), 1365 (m), 1298 (m), 1186 (w), 1060 (m), 1022 (w), 993 (s), 970 (s), 888 (s), 790 (w), 722 (w), 679 (m) cm^{-1}.

$[Co(C_5H_5)]_2[\eta^4,\eta^{4'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$. In a 250 mL, three-neck flask equipped with a magnetic stirring bar, nitrogen inlet, and pressure equalizing dropping funnel, 0.16 g (1.0 mmol) of 3,8-dimethyl-1,3,5,7,9-decapentaene was dissolved in 50 mL of hexane. The flask was cooled to −78 °C, and a solution of 0.37 g (2.0 mmol) of $Co(C_5H_5)(C_2H_4)_2$ in 30 mL of hexane was added slowly to the stirred decapentaene solution. The reaction mixture was initially bright red, but turned a darker red on warming and finally yielded a very intense dark

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red solution. After reaching room temperature, the solution was stirred for an additional 3 h. The solvent was removed in vacuo, and unreacted $Co(C_5H_5)(C_2H_4)_2$ was sublimed out at 35−40 °C. Extraction of the residue with two 40 mL portions of an 80% hexane/20% Et_2O mixture gave a dark red solution, which was filtered through a Celite pad on a coarse frit and concentrated to a volume of 20 mL. After 2 days at −30 °C, 0.24 g (0.59 mmol) of $[Co(C_5H_5)]_2[\eta^4,\eta^{4'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$ was isolated as dark red crystals (mp 173−175 °C). The yield was 59% based on the decapentaene.

This compound was found to exist in two isomeric forms, as evidenced from the NMR spectroscopic studies. The ratio of the two isomers is about one to one. Anal. Calcd for $C_{22}H_{26}Co_2$: C, 64.72; H, 6.42. Found: C, 64.74; H, 6.25. ^1H NMR (benzene-d_6, ambient): δ 6.01 and 5.90 (d of d, J = 7.2, 3.0 Hz, 2H, H-5), 4.71 and 4.68 (d of d, J = 9.0, 6.5 Hz, 2H, H-2), 4.53 and 4.45 (s, 10H, Cp), 2.11 and 2.06 (s, 6H, CH_3), 1.81 and 1.79 (d of d, J = 6.5, 1.8 Hz, 2H, H-1_{exo}), 1.11 and 1.06 (d of d, J = 7.2, 3.0 Hz, 2H, H-4), −0.08 and −0.15 (d of d, J = 9.0, 1.8 Hz, 2H, H-1_{endo}). ^{13}C NMR (benzene-d_6, ambient): δ 132.6 and 132.3 (d, J = 151, 151 Hz, C-5), 90.7 and 90.5 (s, C-3), 81.2 and 81.2 (d, J = 175, 175 Hz, Cp), 77.7 and 77.4 (d, J = 164, 164 Hz, C-2 or 4), 56.5 and 56.3 (d, J = 163, 157 Hz, C-2 or 4), 29.2 and 29.1 (t, J = 156, 157 Hz, C-1), 19.9 and 19.8 (q, J = 124, 127 Hz, CH_3). Mass spectrum (EI, 17 eV) m/z (relative intensity): 409 (22), 408 (91), 406 (12), 340 (14), 338 (11), 283 (35), 189 (100), 151 (13). IR (Nujol mull): 3040 (w), 3005 (m, sh), 1420 (m), 1405 (m), 1344 (m), 1300 (m), 1258 (w), 1180 (m), 1150 (m), 1106 (s), 1098 (m, sh), 1024 (m), 1003 (s), 988 (s), 962 (s), 955 (m), 932 (w), 890 (w), 879 (w), 830 (m), 804 (s), 792 (s), 736 (w), 718 (w), 629 (m) cm^{-1}.

$\{[Co(C_5H_5)]_2[\eta^5,\eta^{5'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]\}(BF_4)_2$, $\{[Co(C_5H_5)]_2[\eta^5,\eta^{5'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]\}(PF_6)_2$. A dark red solution of 0.092 g (0.23 mmol) of $[Co(C_5H_5)]_2[\eta^4,\eta^{4'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$ in 25 mL of methylene chloride was prepared in a 100 mL, three-neck flask equipped with a nitrogen gas inlet, pressure equalizing dropping funnel, and magnetic stirring bar. A deep blue solution of 0.14 g (0.46 mmol) of dimethyl ferricinium tetrafluoroborate,[11] $[Fe(C_5H_4Me)_2](BF_4)$, in 25 mL of methylene chloride was prepared in the dropping funnel. The $[Co(C_5H_5)]_2[\eta^4,\eta^{4'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$ solution was cooled to −78 °C, and the $[Fe(C_5H_4Me)_2](BF_4)$ solution was added dropwise. The reaction mixture was warmed slowly to room temperature, and around −20° the bright red product started to precipitate. Stirring was continued for an additional 2 h after the mixture reached room temperature. The product was allowed to settle before the supernatant was removed via syringe. The product was washed with two 20 mL portions of pentane and dried in vacuo yielding 0.116 g of $\{[Co(C_5H_5)]_2[\eta^5,\eta^{5'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]\}(BF_4)_2$ (quantitative yield).

This dicationic complex may also be prepared as the hexafluorophosphate salt using an analogous method. Thus the reaction of $[Co(C_5H_5)]_2[\eta^4,\eta^{4'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$ with 2 equiv of $[Fe(C_5H_5)_2](PF_6)$ in CH_2Cl_2 resulted in the formation of $\{[Co(C_5H_5)]_2[\eta^5,\eta^{5'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]\}(PF_6)_2$ as a dark red powder in a similar yield.

The powders isolated from either procedure were sufficiently pure for elemental analysis and NMR studies. However, single crystals of the PF_6^- salt were obtained by slow diffusion of CH_2Cl_2 into a concentrated CH_3NO_2 solution over a period of 3 to 4 days. This compound, if isolated as a powder, was found to exist in two isomeric forms in a ratio of ca. 1:1. However, the product isolated from exhaustive, but slow, crystallization through the diffusion process was entirely the trans isomer, as evidenced by NMR spectroscopic and X-ray diffraction studies, apparently indicating that a slow isomerization occurred during crystallization. Anal. Calcd for $C_{22}H_{26}Co_2B_2F_8$: C, 45.41; H, 4.50. Found: C, 45.00; H, 4.58. ^1H NMR (nitromethane-d_3, ambient): Isomer I (trans form): δ 6.24 (d, J = 9.0 Hz, 2H, H-4), 5.71 (t, J = 11.1 Hz, 2H, H-2), 5.54 (s, 10H, Cp), 4.39 (m, overlaps solvent peaks, 2H, H-1_{exo}), 2.68 (d, partially overlaps CH_3 peaks, 2H, H-5), 2.65 (s, 6H, CH_3), 2.21 (d of d, J = 12.0, 3.6 Hz, 2H, H-1_{endo}). Isomer II (cis form): δ 6.11 (d, J = 10.2 Hz, 2H, H-4), 5.68 (t, J = 11.1 Hz, 2H, H-2), 5.58 (s, 10H, Cp), 4.39 (m, overlaps solvent peaks, 2H, H-1_{exo}), 3.05 (d, J = 10.8 Hz, 2H, H-5), 2.69 (s, 6H, CH_3), 2.33 (d of d, J = 12.0, 3.6 Hz, 2H, H-1_{endo}). ^{13}C NMR (nitromethane-d_3, ambient): Isomer I (trans form): δ 117.2 (s, C-3), 96.5 (d, J = 164 Hz, C-2 or 4), 94.7 (d, J = 163 Hz, C-2 or 4), 90.2 (d, J = 174 Hz, Cp), 86.1 (d, J = 168 Hz, C-5), 61.3 (t, J = 160 Hz, C-1), 24.2 (q, J = 130 Hz, CH_3). Isomer II (cis form): δ 116.9 (s, C-3), 96.3 (d, J = 163 Hz, C-2 or 4), 90.2 (d, J = 174 Hz, Cp), 89.6 (d, J = 163 Hz, C-2 or 4), 80.5 (d, J = 168 Hz, C-5), 61.2 (t, J = 160 Hz, C-1), 24.5 (q, J = 130 Hz, CH_3). IR (Nujol mull): 3120 (s), 1431 (m), 1412 (m), 1286 (w), 1205 (w), 1115 (m, sh), 1055 (s, br), 996 (s), 962 (w), 950 (w), 860 (m), 829 (w), 764 (w, sh), 731 (m) cm^{-1}.

$[Ru(C_5Me_5)Cl]_2[\eta^4,\eta^{4'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$. In a 100 mL, three-neck flask equipped with a nitrogen inlet, pressure equalizing dropping funnel, and magnetic stirring bar, 0.42 g (0.39 mmol) of (pentamethylcyclopentadienyl)ruthenium(II) chloride, $[Ru(C_5Me_5)Cl]_4$, was dissolved in 30 mL of THF. The flask was cooled to −78 °C, and a solution of 0.12 g (0.78 mmol) of 3,8-dimethyldecapentaene in 30 mL of THF was added via a dropping funnel. There was no observable reaction at −78 °C. Upon warming to room temperature with stirring, the solution turned a deep red color, and a bright red powder formed. The suspension was kept stirring for an additional hour at room temperature. After the powder had settled, the supernatant was removed via syringe. The product was washed with two 5 mL portions of THF, and 0.50 g (0.71 mmol) of bright red powder (mp 223−225 °C, dec) was thereafter isolated. Additional product (0.03 g) was crystallized from the concentrated supernatant upon cooling to −30 °C for 2 days, giving a total yield of 95%.

This compound exists in two isomeric forms as indicated by the NMR spectroscopic studies. The ratio of the two isomers is approximately two to one. Anal. Calcd for $C_{32}H_{46}Ru_2Cl_2$: C, 54.61; H, 6.59. Found: C, 54.67; H, 6.46. ^1H NMR (methylene chloride-d_2, ambient): Isomer I (major): δ 6.12 (d of d, J = 7.2, 3.3 Hz, 2H, H-5), 4.37 (d of d, J = 9.9, 7.5 Hz, 2H, H-2), 2.91 (d of d, J = 7.5, 1.8 Hz, 2H, H-1_{cis}), 2.49 (d of d, J = 7.2, 3.3 Hz, 2H, H-4), 2.01 (s, 6H, CH_3), 1.62 (s, 30H, CH_3−Cp*), 1.31 (d of d, J = 9.9, 1.8 Hz, 2H, H-1_{trans}). Isomer II (minor): δ 6.34 (d of d, J = 6.9, 3.0 Hz, 2H, H-5), 4.44 (d of d, J = 10.2, 7.8 Hz, 2H, H-2), 2.96 (d of d, J = 7.5, 1.8 Hz, 2H, H-1_{cis}), 2.66 (d of d, J = 6.9, 3.0 Hz, 2H, H-4), 2.10 (s, 6H, CH_3), 1.54 (s, 30H, CH_3−Cp*), 1.38 (d of d, J = 10.2, 1.8 Hz, 2H, H-1_{trans}). ^{13}C NMR (methylene chloride-d_2, ambient): Isomer I (major): δ 129.0 (d, J = 157 Hz, C-5), 103.2 (s, C-3), 94.6 (s, C−Cp*), 88.5 (d, J = 162 Hz, C-2 or 4), 76.5 (d, J = 161 Hz, C-2 or 4), 51.0 (t, J = 163 Hz, C-1), 18.3 (q, J = 127 Hz, CH_3), 9.7 (q, J = 128 Hz, CH_3−Cp*). Isomer II (minor): δ 127.9 (d, J = 154 Hz, C-5), 103.0 (s, C-3), 94.5 (s, C−Cp*), 89.4 (d, J = 161 Hz, C-2 or 4), 75.7 (d, J = 161 Hz, C-2 or 4), 51.6 (t, J = 164 Hz, C-1), 18.1 (q, J = 127 Hz, CH_3), 9.6 (q, J = 128 Hz, CH_3−Cp*). IR (Nujol mull): 3015 (w, sh), 1500 (w, sh), 1362 (m, sh), 1212 (w), 1153 (w), 1068 (m), 1027 (m), 1011 (m), 958 (s), 889 (m), 828 (w), 798 (w), 770 (w), 719 (m) cm^{-1}.

$[Ru(C_5Me_5)]_2[\eta^5,\eta^{5'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$. $[Ru(C_5Me_5)]_2[\eta^5,\eta^{5'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$ was prepared by the reduction of $[Ru(C_5Me_5)Cl]_2[\eta^4,\eta^{4'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$ with 2 equiv of potassium naphthalenide. The 0.1 M solution of potassium naphthalenide was made by the following method. To a 100 mL two-neck flask charged with 0.12 g (3.1 mmol) of potassium sand and 30 mL of THF was added 0.57 g (4.5 mmol) of naphthalene. A dark green solution resulted immediately. This dark green solution was stirred for 3 h to ensure complete conversion before utilization in the subsequent reactions.

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[11] Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. *Inorg. Chem.* **1971**, *10*, 1559.

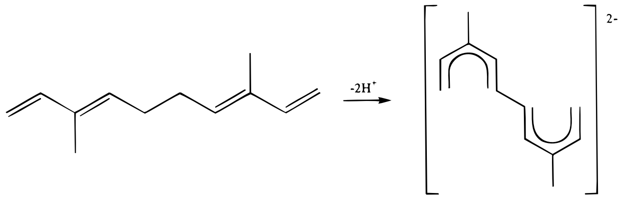
Table 1. X-ray Data Parameters for $Co_2C_{22}H_{26}P_2F_{12}$, $Ru_2C_{32}H_{46}$, and $V_2C_{28}H_{44}P_2$

formula	$Co_2C_{22}H_{26}P_2F_{12}$	$Ru_2C_{32}H_{46}$	$V_2C_{28}H_{44}P_2$
mol. wt.	698.25	632.86	544.50
space group	$P2_1/c$	$P2_1$	$C2/c$
lattice constants			
a (Å)	10.963(1)	10.631(1)	30.813(7)
b (Å)	15.290(2)	11.083(2)	8.292(2)
c (Å)	15.533(2)	12.188(2)	22.281(4)
β (deg)	99.387(4)	93.48(1)	100.14(2)
V (Å^3)	2568.8	1433.3	5604.2
Z	4	2	8
λ (Å)	0.71073	1.54056	1.54056
cryst size (mm)	0.33 × 0.30 × 0.18	0.31 × 0.22 × 0.19	0.39 × 0.33 × 0.06
linear abs coeff (cm^{-1})	15.09	88.50	68.51
rel trans factors	0.878−1.000	0.696−1.000	0.275−1.000
2θ limits (deg)	1−50	4−130	4−100
temp, K	295	295	148
no. of data colld	5108	2731	3227
no. of unique data with $I > n\sigma(I)$; n	3190; 3	2450; 1	1926; 3
$R(F)$	0.060	0.042	0.054
$R_w(F)$	0.067	0.044	0.060
max diff Fourier peak (e/Å^3)	1.13	1.20	0.46

Simultaneously, a flask charged with 0.16 g (0.22 mmol) of $[Ru(C_5Me_5)Cl]_2[\eta^4,\eta^{4'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$ and 50 mL of THF was cooled to −78 °C. The resulting red slurry was carefully titrated with the 0.1 M potassium naphthalenide solution (ca. 4.5 mL) until a yellow solution had formed. After all the solvent was removed in vacuo, the naphthalene formed in the reaction was sublimed out at 30−35 °C. The residue was then extracted with two 40 mL portions of hexane. The combined extracts were filtered through a Celite pad on a frit and concentrated to ca. 15 mL. Upon cooling to −20 °C for 2 days, bright yellow crystals of the title compound formed (mp 192−195 °C, dec). Following removal of the supernatant and drying in vacuo, 0.11 g (0.17 mmol) of $[Ru(C_5Me_5)]_2[\eta^5,\eta^{5'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$ was isolated, corresponding to a yield of 82% based on $[Ru(C_5Me_5)Cl]_2[\eta^4,\eta^{4'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$. Anal. Calcd for $C_{32}H_{46}Ru_2$: C, 60.73; H, 7.33. Found: C, 60.74; H, 7.28. ^{1}H NMR (benzene-d_6, ambient): δ 4.12 (d, J = 7.8 Hz, 2H, H-4), 3.72 (t, J = 8.4 Hz, 2H, H-3), 2.30 (d of d, J = 8.4, 2.7 Hz, 2H, H-1$_{exo}$), 1.94 (s, 6H, CH_3), 1.61 (s, 30H, CH_3−Cp*), 1.45 (d, J = 7.8 Hz, 2H, H-5), 0.43 (d of d, J = 8.4, 2.7 Hz, 2H, H-1$_{endo}$). ^{13}C NMR (benzene-d_6, ambient): δ 96.2 (s, C-3), 88.7 (s, C−Cp*), 83.7 (d, J = 158 Hz, C-2 or 4), 80.8 (d, J = 157 Hz, C-2 or 4), 62.7 (d, J = 160 Hz, C-5), 45.0 (t, J = 154 Hz, C-1), 22.7 (q, J = 126 Hz, CH_3), 10.6 (q, J = 126 Hz, CH_3−Cp*). Mass spectrum (EI, 17 eV) m/z (relative intensity): 638 (14), 637 (15), 636 (49), 635 (44), 634 (92), 633 (86), 632 (100), 631 (98), 630 (97), 629 (83), 628 (76), 627 (54), 626 (42), 625 (27), 624 (22), 398 (24), 397 (14), 396 (10), 331 (15), 329 (24), 328 (15), 327 (10). IR (Nujol mull): 3012 (m), 1585 (w), 1503 (w), 1438 (m, sh), 1425 (m, sh), 1300 (w), 1262 (w), 1212 (m), 1179 (s), 1169 (m, sh), 1140 (m), 1071 (s), 1030 (s), 928 (w), 918 (w), 901 (w), 885 (m), 823 (w, sh), 802 (w), 758 (m), 748 (m), 720 (w), 616 (m) cm^{-1}.

$[V(C_5H_5)(PMe_3)][\eta^5,\eta^{5'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})]$. The $V(C_5H_5)(PMe_3)_2Cl_2$ used in this synthesis was prepared by a published procedure. However, it was found that $V(C_5H_5)(PMe_3)_2Cl_2$ was essentially insoluble in pentane, which was described in the literature as the solvent used to extract the compound. Therefore, a solvent mixture of 60% hexane/40% THF was used to extract and crystallize the $V(C_5H_5)(PMe_3)_2Cl_2$.

Scheme 1



5 6

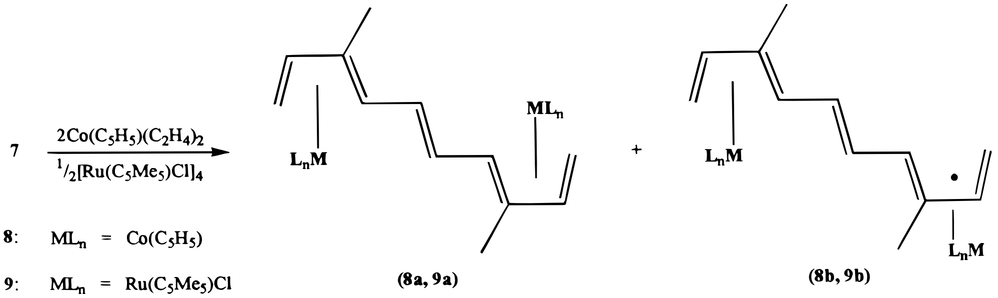
A deep blue solution of $V(C_5H_5)(PMe_3)_2Cl_2$ (0.50 g, 1.5 mmol) in 50 mL of THF was prepared in a 100 mL, three-neck flask and stirred for 4 h over an amalgam made of 0.034 g (1.5 mmol) sodium sand and ca. 0.3 mL of Hg, resulting in a dark purple solution of $[V(C_5H_5)(PMe_3)_2Cl]_2$. This dark purple solution was filtered through a Celite pad into a 250 mL, three-neck flask charged with 0.2 g (excess) of magnesium turnings and equipped with a nitrogen inlet and a pressure equalizing dropping funnel. A solution of 0.12 g (0.75 mmol) of 3,8-dimethyl-1,3,5,7,9-decapentaene in 30 mL of THF was then prepared in the dropping funnel and added to the $[V(C_5H_5)(PMe_3)_2Cl]_2$ solution. The reaction mixture was allowed to stir over the magnesium turnings for 3 days at room temperature. During this time period the color of the solution turned from dark purple to yellow-green, and finally to yellow-brown. After the solvent was removed in vacuo, the residue was extracted with two 40 mL portions of pentane. The combined extracts were filtered through a Celite pad on a frit and concentrated to about 15 mL before cooling to −30 °C. Dark red crystals of the product vanadium complex (mp 128−130 °C) were obtained after cooling for 2 days. Another portion of the compound was isolated from the further concentrated supernatant by cooling to −30 °C for 2 days, giving a total yield of 0.19 g (47% based on $V(C_5H_5)(PMe_3)_2Cl_2$). Anal. Calcd for $C_{28}H_{44}V_2P_2$: C, 61.77; H, 8.14. Found: C, 61.69; H, 8.13. Mass spectrum (EI, 17 eV) m/z (relative intensity): 392 (4, $M^+ - 2(PMe_3)$), 391 (4), 390 (6), 277 (20), 276 (20), 275 (17), 181 (34), 162 (10), 116 (15), 76 (51), 75 (11), 61 (100), 59 (14). ESR data (benzene, ambient): $g = 2.00$; $A_V = 67.8$ G; $A_P = 26.9$ G.

X-ray Diffraction Studies. Single crystals of the cobalt and ruthenium open fulvalene complexes were mounted on glass fibers and covered with epoxy. A crystal of the more air-sensitive vanadium compound was loaded under nitrogen into a glass capillary, which was then flame-sealed. Data were collected on a Nicolet-Siemens P$\bar{1}$ autodiffractometer for the cobalt complex, but on an Enraf-Nonius autodiffractometer for the others. In each case, the metal atom positions were established from a Patterson map, and subsequent difference Fourier maps revealed the positions of the remaining non-hydrogen atoms, which were subsequently subjected to anisotropic refinement. For the cobalt and vanadium complexes, most hydrogen atom locations could also be determined, and these atoms were then included in idealized positions. Other pertinent data collection and structural solution parameters are included in Table 1.

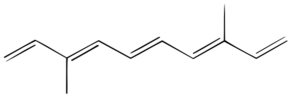
Results and Discussion

From the coupling of 3-methylpentadienyl radicals one can selectively isolate 3,8-dimethyl-1,3,7,9-decatet-

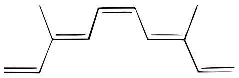
Scheme 2



raene (**5**) as a colorless oil in 81% yield. Subsequent deprotonation with 2 equiv of $KO(t\text{-}C_4H_9)/(n\text{-}C_4H_9Li)$ then leads to the expected dianion (**6**) as a potassium salt in apparently high isolated yields (Scheme 1). Although free pentadienyl anions of this sort tend to favor the W conformation,[12] in the presence of the potassium ion (or with 2,4-disubstitution) the depicted *U* geometry may become favored.[13] Several attempts to prepare open fulvalene complexes from this dianion have not been successful, perhaps due to its greater susceptibility to redox and proton-transfer reactions. Attempts were then made to oxidize the dianion to a neutral pentaene. Indeed, reaction of the dianion with $ZnCl_2$ leads to 3,8-dimethyl-1,3,5,7,9-decapentaene (**7**) as a pungent, volatile, crystalline solid, although only in ca. 19% yield. This pentaene has been characterized straightforwardly (see the Experimental Section) and is presumed to exist as the all-trans form **7a**, although forms such as **7b** cannot be entirely excluded. In fact, minor NMR peaks are found near those of the major ones, likely indicating the presence of at least one other isomer in small quantities.



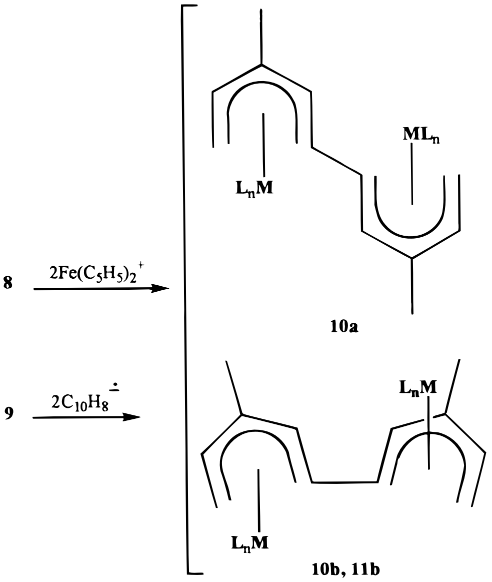
7a



7b

The pentaene does readily coordinate its two terminal dienes to appropriate metal fragments, such as $Ru(C_5Me_5)Cl$ or $Co(C_5H_5)$. Thus, reactions with $[Ru(C_5Me_5)Cl]_4$ and $Co(C_5H_5)(C_2H_4)_2$ lead to the desired products, each as a mixture of two isomers (Scheme 2), as judged by NMR spectroscopy. Somewhat similar species have been reported in which two $Fe(CO)_3$ groups are coordinated by the terminal diene fragments from 2,4,6,8,10-dodecapentaene,[14] although an attempt to prepare a related dicationic $\eta^5,\eta^{5'}$ complex through a formal double hydride abstraction from a ($\eta^4,\eta^{4'}$-2,4,7,9-tetramethyl-1,3,7,9-decatetraene)$Fe_2(CO)_6$ complex led instead to a central C−C bond cleavage, yielding 2 equiv of $Fe(2,4\text{-}C_7H_{11})(CO)_3^+$ (C_7H_{11} = dimethylpentadienyl).[15] The presence of central, uncoordinated C=C bonds in **8** and **9** is readily evident from a single downfield resonance in both the ^1H and ^{13}C NMR spectra for each species.

Scheme 3



For the cobalt products, a ratio of ca. 1.6−1.7:1 is observed, while for ruthenium the products are observed in a 2:1 ratio. While products **8b** and **9b** are depicted in their syn forms, as the metal centers are on the same side of the diene, it can be expected that rotation about the C4−C5 or C6−C7 single bonds would occur in order to increase the separation between the two coordination spheres. In any event, some support for the depicted structures could be obtained for at least the major isomers through the observation of the nuclear Overhauser effect on irradiation of their methyl resonances. Upon such irradiation, one observes selective enhancement of the proton signals attached to the carbon atoms in the 2 and 5, but not 4, positions, confirming the structural assignment.

Conversion of the $\eta^4,\eta^{4'}$ complexes **8** and **9** to $\eta^5,\eta^{5'}$ open fulvalene complexes could be effected by the respective two-electron oxidation or reduction reactions, yielding complexes **10** ($ML_n = Co(C_5H_5)^+$) and **11** ($ML_n = Ru(C_5Me_5)$, Scheme 3). These were characterized through standard spectroscopic and analytical methods. Especially characteristic of the conversion from $\eta^4,\eta^{4'}$ to $\eta^5,\eta^{5'}$ coordination was the loss of the downfield signals for the free, central −CH=CH− units in the ^1H and ^{13}C NMR spectra. As for **8**, **10** was isolated as a mixture, although in a more nearly equal ratio (ca. 1.1−1.2:1). However, for **11**, only a single isomer was readily apparent spectroscopically. Structural determinations for **10a** and **11b** have further confirmed these formulations (vide infra).

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[12] (a) Bates, R. B.; Gosselink, D. W.; Kaczynski, J. A. *Tet. Lett.* **1967**, *3*, 205. (b) Ernst, R. D. *Struct. Bond.* (*Berlin*) **1984**, *57*, 1.

[13] Schlosser, M.; Rauchschwalbe, G. *J. Am. Chem. Soc.* **1978**, *100*, 3258.

[14] Hafner, A.; Bieri, J. H.; Prewo, R.; v. Phillipsborn, W.; Salzer, A. *Angew. Chem., Intl. Ed. Engl.* **1983**, *22*, 713.

[15] Rheingold, A. L.; Haggerty, B. S.; Ma, H.; Ernst, R. D. *Acta Crystallogr.* **1996**, *C52*, 1110.

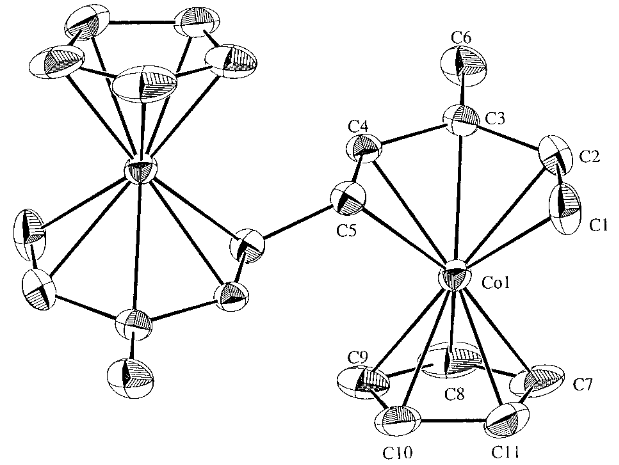
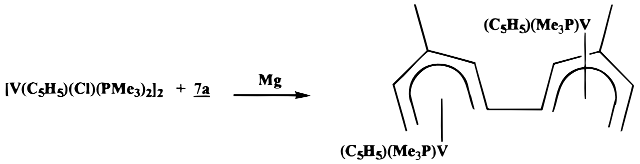


Figure 1. Perspective view of $[\eta^5,\eta^{5'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})][Co(C_5H_5)]_2^{2+}$.

Scheme 4



An alternative approach has been utilized to prepare a paramagnetic open fulvalene complex. As $V(C_5H_5)(\eta^4\text{-}C_4H_6)(PMe_3)$ has been prepared through the reduction of $V(C_5H_5)(Cl)_2(PMe_3)_2$ in the presence of butadiene,[16] a similar approach has been employed utilizing pentaene **7a**, with the partially prereduced $[V(C_5H_5)(Cl)(PMe_3)_2]_2$ (Scheme 4).

The formulation for this compound has been confirmed through a single-crystal diffraction study (vide infra). The vanadium centers in this complex have a 17-electron configuration, and the resulting complex is indeed paramagnetic, exhibiting a 16-line pattern due to couplings to both the vanadium ($I = 7/2$ and phosphorus ($I = 1/2$) nuclei, with g, A_V, and A_P values of 2.00, 67.8 G, and 26.9 G, respectively, matching quite closely the values observed previously for half-open vanadocenes (ca. 1.99, 67−69 G, and 27−30 G, respectively).[17] The ESR data thus do not provide any indication of the presence of a second isomer (cf., **10a**) or of any magnetic coupling between the two metal centers. However, in contrast to the typically green half-open vanadocenes, this complex is dark red-brown, perhaps an indication of some interaction between the two metal centers, at least in an excited, if not the ground, state.

The structure of one isomer of the dicobalt open fulvalene complex has been determined and is shown in Figure 1, while important bonding parameters are given in Table 2. It can be seen that this corresponds to isomer **10a**, with crystallographically imposed C_i symmetry. Actually, there are two independent half-molecules in the asymmetric unit, but their structural parameters are essentially identical and generally similar to those observed in $Co(C_5H_5)(2,4\text{-}C_7H_{11})BF_4$.[18] The average Co−C ($C_5H_5$) distance of 2.049(6) Å appears shorter than those for the fulvalene ligands, which average[19] 2.074 Å. Even so, the average Co−dienyl plane distance of 1.442 Å is significantly shorter than that of 1.664 Å for the C_5H_5 ligands, as a result of the greater girth of the former. The shortest Co−C (pentadienyl) distances involve the C[2,4] positions, 2.029(2) Å, while those for the C[1], C[3], and C[5] positions average 2.086(4), 2.071(3), and 2.154(3) Å, respectively. The C−C distances for the isolated open dienyl fragments are normal, with the external ones appearing shorter than the internal ones, 1.406(3) vs 1.417(3) Å. The C[5−5′] distances average 1.454(6) Å, similar to values for fulvalene complexes themselves[20] and apparently reflecting some degree of favorable π overlap between the two dienyl fragments. With imposed C_i symmetry, the two dienyl fragments must lie in parallel planes, which should promote favorable π overlap. However, the planes are separated by ca. 0.4 Å as a result of a C[3]−C[4]−C[5]−C[5′] torsion angle of 15.6°. The C[6] atoms are also tilted below the dienyl ligand plane, by an average of 1.6°, and there is an average angle of 9.1° between the C_5H_5 and open dienyl planes.

Table 2. Pertinent Bond Distances and Angles for $Co_2C_{22}H_{26}P_2F_{12}$

Bond Distances (Å)			
Co1−C1	2.088(5)	Co2−C1′	2.085(5)
Co1−C2	2.028(5)	Co2−C2′	2.024(5)
Co1−C3	2.073(4)	Co2−C3′	2.069(4)
Co1−C4	2.032(4)	Co2−C4′	2.033(4)
Co1−C5	2.146(4)	Co2−C5′	2.163(4)
Co1−C7	2.035(5)	Co2−C7′	2.035(5)
Co1−C8	2.085(5)	Co2−C8′	2.041(5)
Co1−C9	2.058(5)	Co2−C9′	2.072(5)
Co1−C10	2.040(5)	Co2−C10′	2.055(5)
Co1−C11	2.027(5)	Co2−C11′	2.044(5)
C1−C2	1.398(7)	C1′−C2′	1.400(7)
C2−C3	1.418(7)	C2′−C3′	1.417(7)
C3−C4	1.419(6)	C3′−C4′	1.414(6)
C3−C6	1.500(6)	C3′−C6′	1.490(7)
C4−C5	1.413(6)	C4′−C5′	1.413(6)
C5−C5a	1.462(8)	C5′−C5a′	1.447(8)
C7−C8	1.386(10)	C7′−C8′	1.426(8)
C7−C11	1.431(8)	C7′−C11′	1.393(8)
C8−C9	1.398(8)	C8′−C9′	1.368(9)
C9−C10	1.418(8)	C9′−C10′	1.408(9)
C10−C11	1.412(8)	C10′−C11′	1.398(8)
Bond Angles (deg)			
C1−C2−C3	124.6(4)	C1′−C2′−C3′	125.6(4)
C2−C3−C4	122.5(4)	C2′−C3′−C4′	122.1(4)
C2−C3−C6	117.9(4)	C2′−C3′−C6′	118.3(4)
C3−C4−C5	125.6(4)	C3′−C4′−C5′	126.0(4)
C4−C3−C6	118.8(4)	C4′−C3′−C6′	118.8(5)
C4−C5−C5a	118.9(5)	C4′−C5′−C5a′	119.7(5)
C7−C8−C9	107.7(5)	C7′−C8′−C9′	108.2(5)
C7−C11−C10	106.4(6)	C7′−C11′−C10′	107.4(5)
C8−C7−C11	109.3(5)	C8′−C7′−C11′	107.8(6)
C8−C9−C10	108.8(6)	C8′−C9′−C10′	108.1(6)
C9−C10−C11	107.7(5)	C9′−C10′−C11′	108.6(5)

Attempts were made to isolate the second ($\eta^{5,5'}$-open fulvalene)dicobalt isomer by exhaustive crystallization of a solution containing the mixture of isomers. How-

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[16] Hessen, B.; Meetsma, A.; Bolhuis, F. V.; Teuben, J.; Helgesson, G.; Jagner, S. *Organometallics* **1990**, *9*, 1925.

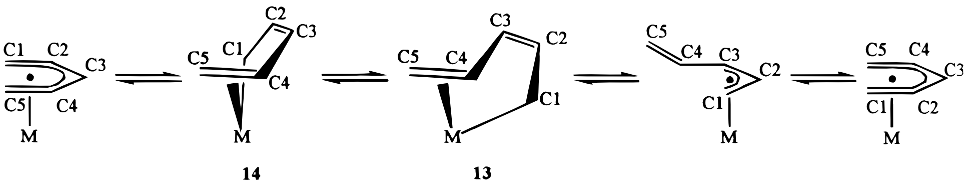
[17] Gedridge, R. W.; Hutchinson, J. P.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1993**, *12*, 1553.

[18] Ernst, R. D.; Ma, H.; Sergeson, G.; Zahn, T.; Ziegler, M. L. *Organometallics* **1987**, *6*, 848.

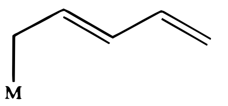
[19] An esd of 0.001 Å for the average value can be derived on the basis of the esd's of the individual values. This esd will reflect the uncertainty in the average value, but not the distribution of the individual values, which vary significantly.

[20] Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1969**, *8*, 1970.

Scheme 5



ever, NMR characterization of the crystalline material (grown slowly at room temperature) continually showed the presence of only the major isomer, suggesting the occurrence of an isomerization process through which the metal-bound and unbound dienyl faces could change places. Although the most obvious mechanism through which this could occur would involve an η^1-bound dienyl ligand, **12**, one would likely expect such a process, leading to a 14-electron intermediate, to encounter a significant barrier. A more subtle mechanism involves an unusual η^3 intermediate, in which the metal center is attached through the 1, 4, and 5 dienyl positions. Such bonding has actually been observed for both tantalum[21] and iridium[22] complexes (approximating forms **13** and **14**, respectively), and the process outlined in Scheme 5 would thus require only a conversion to a 16-electron complex for isomerization to occur for the (open fulvalene)dicobalt complex. Notably, a change in endo and exo substituents would occur for the σ-bound carbon atom in intermediate **13**, but not for the other terminal carbon atom. Thus, for the (open fulvalene)dicobalt complex, the isomerization process would require the η^3 intermediate to have the cobalt center σ bound to the terminal dienyl carbon atom, so that the exchanging endo/exo substituents would each be hydrogen atoms. A related process has already been observed for (diene)metal complexes, through which both endo/exo substituent pairs undergo exchange.[23] Furthermore, recent observations have demonstrated that the two isomers of Fe(2,3-dimethylpentadienyl)$_2$ undergo interconversion, presumably also through an η^3 intermediate such as that of Scheme 5, with observable changes in composition occurring within hours at room temperature.[24]



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In contrast to the situation for cobalt, the ruthenium open fulvalene complex was only observed spectroscopically in a single isomeric form. A structural determination has revealed that in this case the formal C$_2$ isomer is adopted, **11b**. The structure of the complex appears in Figure 2, while important bonding parameters are contained in Table 3. Similar to the cobalt complex, one observes that the two dienyl planes are tilted toward each other, in this case by ca. 21.5°. The tilt does not originate with the central C5−C6 bond, whose torsion angle (2.5°) is the smallest of all those associated with the C1−C10 fragment, while those for the adjacent bonds are greatest, averaging −167.3°, reflecting a rather normal tilt of ca. 12.7° by C5 and C6

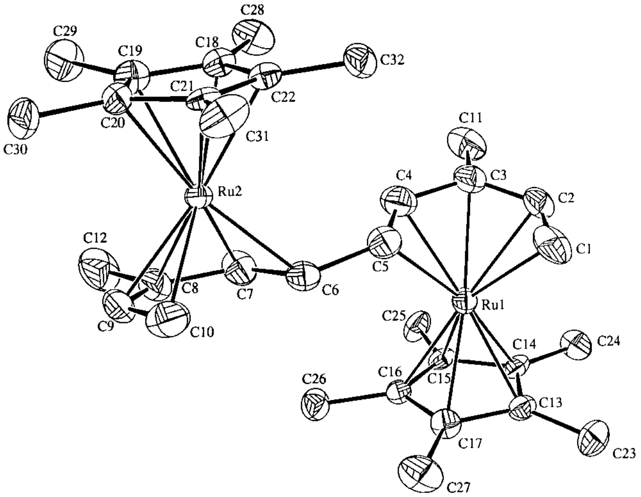

Figure 2. Solid-state structure of $[\eta^5,\eta^{5'}\text{-}3,8\text{-}(CH_3)_2(C_{10}H_{10})][Ru(C_5Me_5)]_2$.

Table 3. Pertinent Bond Distances and Angles for $Ru_2C_{32}H_{46}$

Bond Distances (Å)			
Ru1−C1	2.219(13)	Ru2−C6	2.264(11)
Ru1−C2	2.127(11)	Ru2−C7	2.153(12)
Ru1−C3	2.167(12)	Ru2−C8	2.148(13)
Ru1−C4	2.117(13)	Ru2−C9	2.142(11)
Ru1−C5	2.258(11)	Ru2−C10	2.204(11)
Ru1−C13	2.203(10)	Ru2−C18	2.207(10)
Ru1−C14	2.194(11)	Ru2−C19	2.169(11)
Ru1−C15	2.253(10)	Ru2−C20	2.179(12)
Ru1−C16	2.198(10)	Ru2−C21	2.191(11)
Ru1−C17	2.181(11)	Ru2−C22	2.209(10)
C1−C2	1.395(20)	C13−C14	1.403(14)
C2−C3	1.385(17)	C13−C17	1.442(14)
C3−C4	1.475(16)	C13−C23	1.500(14)
C4−C5	1.354(18)	C14−C15	1.453(12)
C5−C6	1.477(14)	C15−C16	1.426(13)
C6−C7	1.397(17)	C16−C17	1.408(14)
C7−C8	1.441(16)	C18−C19	1.412(14)
C8−C9	1.369(18)	C18−C22	1.431(14)
C9−C10	1.476(21)	C19−C20	1.419(15)
C3−C11	1.474(19)	C20−C21	1.420(13)
C8−C12	1.481(19)	C21−C22	1.406(13)
Bond Angles (deg)			
C1−C2−C3	126.7(13)	C13−C14−C15	109.4(9)
C2−C3−C4	118.3(12)	C13−C17−C16	108.1(8)
C3−C4−C5	130.6(13)	C14−C13−C17	107.2(8)
C4−C5−C6	122.9(12)	C14−C15−C16	105.7(8)
C5−C6−C7	123.5(12)	C15−C16−C17	109.5(8)
C6−C7−C8	125.6(12)	C18−C19−C20	108.8(9)
C7−C8−C9	124.3(12)	C18−C22−C21	108.0(8)
C8−C9−C10	124.7(10)	C19−C18−C22	107.3(9)
C2−C3−C11	120.9(12)	C19−C20−C21	107.2(8)
C4−C3−C11	119.9(12)	C20−C21−C22	108.7(9)
C7−C8−C12	118.6(13)	C9−C8−C12	116.6(12)

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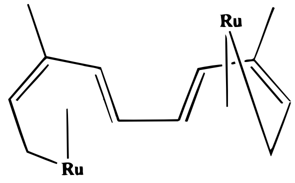
[21] Arif, A. M.; Ernst, R. D.; Meléndez, E.; Rheingold, A. L.; Waldman, T. E. *Organometallics* **1995**, *14*, 1761.

[22] Bleeke, J. R.; Boorsma, D.; Chiang, M. Y.; Clayton, T. W., Jr.; Haile, T.; Beatty, A. M.; Xie, Y.-F. *Organometallics* **1991**, *10*, 2391.

[23] (a) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6346. (b) Eaton, D. B.; King, J. A., Jr.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1359.

[24] Turpin, G. C.; Ernst, R. D. Unpublished results.

from the adjacent dienyl planes,[25] toward the ruthenium center. The tilts of C11 and C12 occur in the same direction, but are smaller, averaging 4.2°. The source of the major tilt between the dienyl fragments might be a result of an attempt to optimize π overlap between the two fragments, while retaining the normal tilt of C6 or C5 below their adjacent dienyl planes. This is evidenced by the long/short alternation in the carbon−carbon bond lengths in the C1−C10 fragment, which would be consistent with a significant contribution from a resonance hybrid such as **15**, containing a fully conjugated tetraene. Such a pattern was not observed for the isolated cobalt isomer, perhaps due either to its change in form (i.e., being **10a** instead of **10b**) or its higher charge or oxidation state. This pattern also was not found for a vanadium complex either, probably due to a twist between dienyl fragments (vide infra), which would greatly reduce conjugation. The C5−C6 distance of 1.477(14) Å is again comparable to values observed for fulvalene(dimetal) complexes. As is generally observed, the presence of a methyl group on a dienyl carbon atom has led to a smaller bond angle involving the adjacent delocalized carbon atoms.[26]



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The C_5Me_5 ligands are fairly planar, with the methyl groups tilted away from the metal centers, by values ranging from 1.7 to 5.8°. An average Ru−C(C_5Me_5) distance of 2.198(7) Å is observed, whereas the Ru−C(open fulvalene) distances may be grouped into five categories, with the appropriate respective distances to C(1,10), C(2,9), C(3,8), C(4,7), and C(5,6) being 2.211(8), 2.134(8), 2.158(9), 2.135(9), and 2.261(8) Å. An overall average of 2.180(4) Å therefore results, seemingly shorter than the average for the C_5Me_5 ligand, consistent with earlier observations.[27] As the usual result of the greater girth of the open dienyl fragment, the average Ru−C_5Me_5 plane separation of 1.836 Å is significantly longer than the value of 1.592 Å for the open dienyl plane.

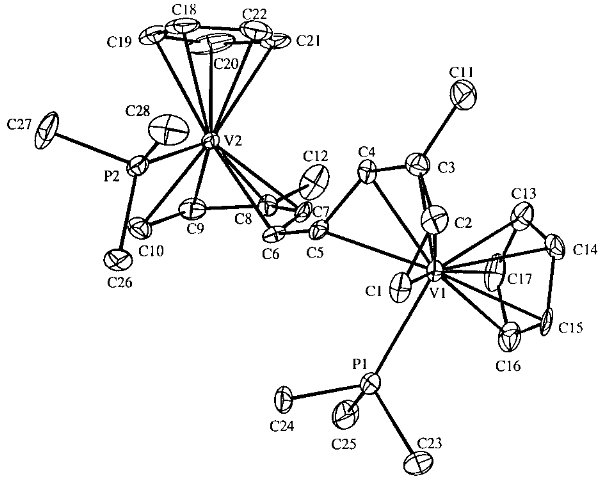

Figure 3. Perspective view of [$\eta^5,\eta^{5'}$-3,8-$(CH_3)_2(C_{10}H_{10})$]-[$V(C_5H_5)(PMe_3)$]$_2$.

Table 4. Pertinent Bond Distances and Angles for $V_2C_{28}H_{44}P_2$

Bond Distances (Å)			
V1−P1	2.411(2)	V2−P2	2.407(2)
V1−C1	2.190(8)	V2−C6	2.291(6)
V1−C2	2.165(8)	V2−C7	2.187(7)
V1−C3	2.220(8)	V2−C8	2.220(8)
V1−C4	2.217(7)	V2−C9	2.143(8)
V1−C5	2.299(6)	V2−C10	2.193(7)
V1−C13	2.256(7)	V2−C18	2.296(8)
V1−C14	2.259(7)	V2−C19	2.283(7)
V1−C15	2.285(7)	V2−C20	2.257(8)
V1−C16	2.322(8)	V2−C21	2.263(8)
V1−C17	2.326(8)	V2−C22	2.291(9)
C1−C2	1.400(11)	C13−C14	1.421(11)
C2−C3	1.429(11)	C13−C17	1.409(12)
C3−C4	1.421(10)	C14−C15	1.403(11)
C4−C5	1.404(9)	C15−C16	1.425(11)
C5−C6	1.504(10)	C16−C17	1.396(12)
C6−C7	1.410(10)	C18−C19	1.396(12)
C7−C8	1.413(10)	C18−C22	1.368(13)
C8−C9	1.408(10)	C19−C20	1.379(13)
C9−C10	1.399(10)	C20−C21	1.416(15)
C3−C11	1.531(11)	C21−C22	1.362(15)
C8−C12	1.527(10)		

Bond Angles (deg)			
C1−C2−C3	126.5(8)	C13−C14−C15	107.5(7)
C2−C3−C4	125.4(7)	C13−C17−C16	107.4(8)
C3−C4−C5	127.5(7)	C14−C13−C17	108.7(7)
C4−C5−C6	121.7(6)	C14−C15−C16	107.6(7)
C5−C6−C7	120.5(6)	C15−C16−C17	108.9(8)
C6−C7−C8	128.3(6)	C18−C19−C20	106.3(8)
C7−C8−C9	124.4(7)	C18−C22−C21	107.7(10)
C8−C9−C10	128.0(7)	C19−C18−C22	110.0(9)
C2−C3−C11	116.2(7)	C19−C20−C21	107.9(9)
C4−C3−C11	118.1(7)	C20−C21−C22	108.1(9)
C7−C8−C12	117.1(6)	C9−C8−C12	117.9(7)

The structure of the isolated vanadium open fulvalene isomer (Figure 3 and Table 4) matches that of the ruthenium complex, with idealized C_2 symmetry. However, unlike either of the other structures, the two open dienyl planes are severely twisted relative to each other, with the angle between them being 53.5°, primarily due to rotation about the C5−C6 bond, whose torsion angle is 37.5°. The origin of the substantial twist can be traced to the presence of the PMe_3 ligands, which would collide with each other as planarity is approached. This twist may be responsible for two other features, a seemingly long C5−C6 bond (1.504(10) Å) and a relatively small tilt of 6.7° by C6 and C5 from their adjacent dienyl planes. A more normal tilt would serve to bring the PMe_3 ligands into closer proximity.

Each formal half-open vanadocene unit exhibits a reasonable geometry, with the tilt between the open and closed dienyl ligands averaging 23.1°, while the V−P vector makes angles of 3.3° and 19.4°, respectively, with these two planes. The methyl substituents undergo only very small tilts of ca. 0.1° toward the metal center, a

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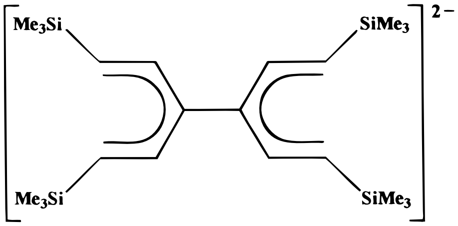
[25] A similar tilt of 12.0° can also be derived, on the basis of the average deviation of 0.307 Å of C5 and C6 from their adjacent planes and the C5−C6 distance.

[26] (a) Ernst, R. D. *Struct. Bond.* (*Berlin*) **1984**, *57*, 1. (b) Bock, H.; Ruppert, K.; Näther, C.; Havlas, Z.; Hermann, H.-F.; Arad, C.; Göbel, I.; John, A.; Meuret, J.; Nick, S.; Rauschenbach, A.; Seitz, W.; Vaupel, T.; Solouki, B. *Angew. Chem. Intl. Ed. Engl.* **1992**, *31*, 550.

[27] (a) Stahl, L.; Ernst, R. D. *Organometallics* **1983**, *2*, 1229. (b) Trankarnpruk, W.; Arif, A. M.; Ernst, R. D. *Organometallics* **1992**, *11*, 1686. (c) Bosch, H. W.; Hund, H.-U.; Nietlispach, D.; Salzer, A. *Organometallics* **1992**, *11*, 2087. (d) Kirss, R. U.; Quazi, A.; Lake, C. H.; Churchill, M. R. *Organometallics* **1993**, *12*, 4145.

possible result of decent overlap between the dienyl ligand and the large vanadium center. As in V(C_5H_5)(C_5H_7)(PEt$_3$),[17] the V−C (open dienyl) distances are significantly shorter on average than those for the C_5H_5 ligand, 2.212(2) vs 2.284(3) Å. Because of the greater girth of the open ligand, this translates to a much greater difference between the metal center and the ligand plane, 1.574 vs 1.950 Å.

The accessibility of open fulvalene ligands now allows for the preparations and study[28] of a greater variety of dimetal complexes in which there is a potential for electronic and magnetic metal−metal interactions. Although the preparation of the 3,8-dimethyl-1,3,5,7,9-decapentaene is somewhat tedious, the related 2,4,6,8,-10-dodecapentaene appears much more straightforward to prepare, through McMurray coupling of sorbyl aldehyde.[29,30] In addition, two potential center−center-coupled open fulvalene ligand sources have also been prepared (**16**, **17**) utilizing the 1,5-bis(trimethylsilyl)pentadienyl anion as the starting material.[31−33] We will report our results in these areas in due course.



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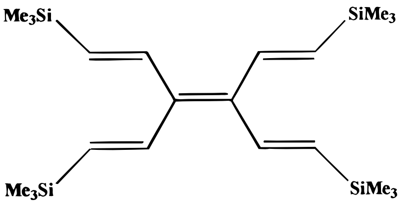

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Acknowledgment. R.D.E. is grateful to the NSF for partial support of this work.

Supporting Information Available: Tables of positional coordinates, anisotropic thermal parameters, torsion angles, and least-squares planes (47 pages). Ordering information is given on any current masthead page.

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[28] (a) Dication(s) **10** exhibit(s) a single reversible reduction wave in the range +1.00 to −1.30 V at $E_{1/2} = -0.78$ V vs ferrocene in THF at a glassy carbon electrode.[28b] (b) Trupia, S.; Vos, D.; Geiger, W. E. Personal communication.

[29] Boone, D. R.; Ernst, R. D. Unpublished results.

[30] See also: (a) Bohlmann, F. *Chem. Ber.* **1952**, *85*, 386. (b) Hayashi, T.; Sasaoka, K.; Oishi, T. *Chem. Commun.* **1990**, 1362.

[31] Yasuda, H.; Nishi, T.; Lee, K.; Nakamura, A. *Organometallics* **1983**, *2*, 21.

[32] (a) Oxidative coupling of the anion leads to a structurally characterized dimer, which yields **16** on deprotonation. Oxidation of **16** by Fe(C_5H_5)$_2^+$ or quinones then leads to **17**.[32b] (b) Weng, W.-Q.; Trankarnpruk, W.; Ernst, R. D.; Rheingold, A. L. Unpublished results.

[33] For similar species see also: (a) Doering, W.v. E.; Birladeanu, L.; Sarma, K.; Shao, L.-S. *J. Am. Chem. Soc.* **1996**, *118*, 6660. (b) Rubin, Y.; Knobler, C. B.; Diedrich, F. *Ang. Chem. Intl. Ed.* **1991**, *30*, 698.