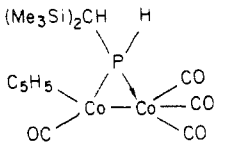
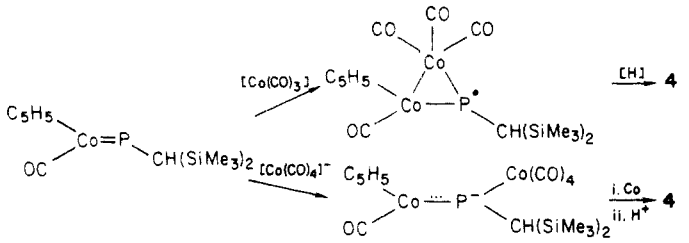
The red crystalline product of the $Na[Co_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ reaction was identified as the Co_2P ring compound 4 by X-ray diffraction methods (Figure 2).[8] Although the



4

hydrogen on phosphorus was not evident in the X-ray study, its presence was established by the detection of a parent peak in the EI mass spectrum and by the diamagnetism of the compound.[13] Moreover, even though $^{31}P\text{–}^{1}H$ coupling could not be detected in the ^{31}P NMR spectrum due to the breadth of the signal, the chemical shift of +144 ppm is consistent with the phosphido bridge formulation. We do not have any evidence regarding the mechanism of formation of 4. However, it is possible that this compound arises from an initially formed terminal phosphinidene complex via either of the mechanisms shown.[14] The source of the $Co(CO)_3$ unit is presumable



the $[Co(CO)_4]^-$ anion which is always present in solutions of $Na[Co_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$.[7]

Acknowledgment. We are grateful to the National Science Foundation, the Robert A. Welch Foundation, and the Science and Engineering Research Council for financial support.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for 2, 3, and 4 (59 pages). Ordering information is given on any current masthead page.

(13) As is clear from the ratio of the number of observed to the number of total reflections, the crystals of 4 did not diffract strongly. We can, however, detect the hydrogen on phosphorus in the recently prepared analogue $Co_2[\mu\text{-}P(H)CH(SiMe_3)_2](\eta^5\text{-}C_5Me_5)(CO)_4$, and the P–H bond length is 1.36 (9) Å. Arif, A. M.; Cowley, A. H.; Pakulski, M., to be submitted for publication.

(14) We are indebted to a reviewer for suggesting the ionic mechanism.

Bis(triphenylphosphine)platinum Complexes of Cycloheptatetraene, Benzocycloheptatetraene, and Dibenzocycloheptatetraene

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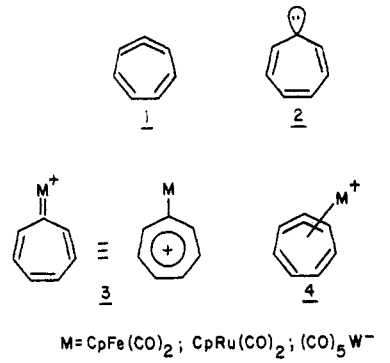
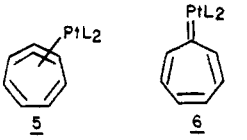
Summary: Addition of a mixture of isomeric bromocycloheptatrienes, 1,2-benzo-4-bromocycloheptatriene, or 1,2,3,4-dibenzo-6-bromocycloheptatriene to a THF solution of tris(triphenylphosphine)platinum and potassium *tert*-butoxide gives the corresponding cycloheptatetraene complexes **7**, **8**, and **9**. These are the first such complexes to exist in the allene form; all previous examples preferred tropylium ion structures.

It is now well established that allene 1 is energetically preferred over its planar isomer 2 while in complexes of this ligand with Fe(II), Ru(II), or W(0), the opposite preference is shown; 3 is favored over 4.[1–9] This change

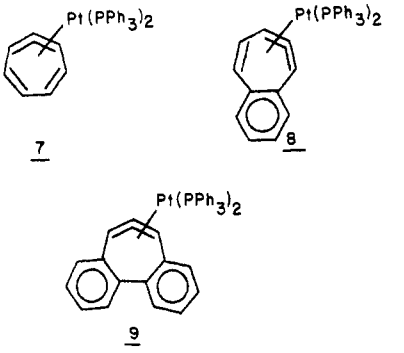


M = $CpFe(CO)_2$; $CpRu(CO)_2$; $(CO)_5W^-$

in structural preference is convincingly rationalized for the Fp^+ (Fp = (η^5-cyclopentadienyl)dicarbonyliron) complex by EHMO calculations which forecast the carbene (or tropylium) structure to lie significantly below its allene isomer.[10] Calculations at the same level make the interesting prediction that the structural preference should be reduced to no difference for the corresponding $(H_3P)_2Pt$ complex. We took these results to suggest that a Pt(0) complex of C_7H_6 might prefer structure 5 over 6. At this



time we report the synthesis of 7–9, all of which exist exclusively as allene complexes.



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(10) Details of this work will be published elsewhere.

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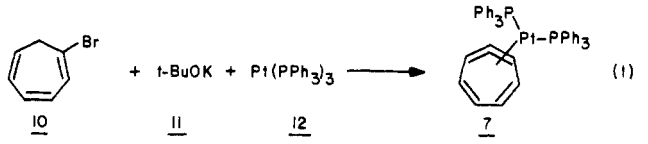
Table I. Selected NMR Data for Allene Complexes I–III[a–d]

compd.	^{1}H NMR	^{13}C NMR	^{31}P
7	2.94 (J_{PtH} = 70.4, J_{PH} = 11)	27.7 (J_{PC} = 5.1, 44.1)	31.5 (J_{PP} = 33.3, J_{PtP} = 3267)
	4.63 (J_{PtH} = 70.8, J_{PH} = 9.7)	114.5 (J_{PC} = 9.3, 5.6, J_{PtC} = 0)	
		151.0 (J_{PC} = 10.4, 61.0)	27.3 (J_{PtP} = 3170)
8	3.02 (J_{PtH} = 72, J_{PH} = 13.2)	26.4 (J_{PC} = 4.9, 43.9)	30.5 (J_{PP} = 30.1, J_{PtP} = 3297)
	5.16 (J_{PtH} = 66, J_{PH} = 9, 4.5)	113.0 (J_{PC}[e])	
		156.1 (J_{PC} = 9.7, 62.3)	26.2 (J_{PtP} = 3131)
9	3.48 (J_{PtH} = 70.8)	29.5 (J_{PC} = 5.4, 52.2)	29.0 (J_{PP} = 28, J_{PtP} = 3208)
	5.71 (J_{PtH} = 54.6, J_{PH} = 8.4, 2.8)	109.9 (J_{PC} = 5.3, 10, J_{PtC} = 0)	
		164.4 (J_{PC} = 9.6, 62.9)	27.5 (J_{PtP} = 3145)

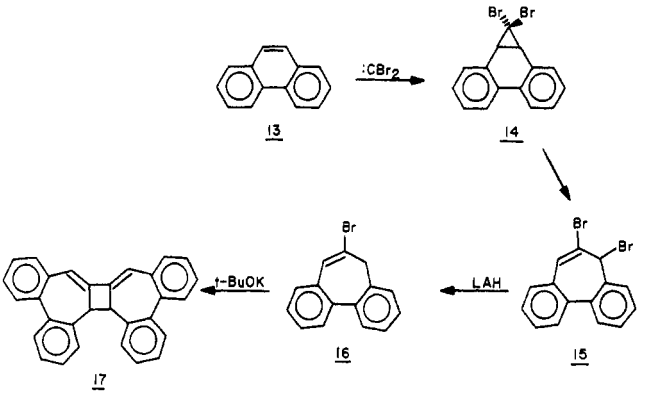
[a] All spectra were recorded in $CDCl_3$; shifts are in ppm. [b] Coupling constants are recorded in Hz. [c] Only signals from the allene functionality are reported. [d] Due to instrument time limitations, in most cases, the spectra were not resolved enough for PtC coupling constants to be observed. [e] These P–C coupling constants could not be measured because of overlapping signals.

The allene complexes were prepared by trapping the allenes (generated in situ) with $Pt(PPh_3)_3$[11,12] (eq 1). The

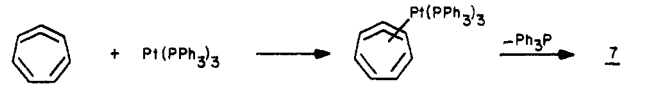


parent and monobenzoannelated allene were generated by known methods.[1,14] The dibenzoannelated allene had not been previously reported and was prepared as outlined in

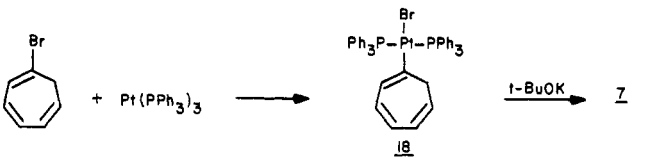
Scheme I



Scheme II



Scheme III



Scheme I.[15] The generation of the dibenzoannelated allene was confirmed by characterization of its dimer, 17. Structure assignments for each of the allene complexes are based on ^{1}H, ^{13}C, and ^{31}P NMR and C, H analyses.[11] The most pertinent spectral data are summarized in Table I. The spectral data compare well with values reported for allene complexes of $Pt(PPh_3)_2$.[16,17] The observed nonequivalence of phosphorus atoms assures that the allene complexes are not fluxional at room temperature; this also requires that none are in equilibrium (on an NMR time scale) with the carbene form 6. To explore this possibility further, variable-temperature NMR studies were carried out on the parent complex (the complex for which interconversion should be the most rapid). Upon heating to 80 °C, no change was observed in the ^{1}H NMR spectrum. This is equivalent to a fluxionality barrier and, in turn, an isomer interconversion barrier of at least 17 kcal/mol.[18]

By analogy with the preparation of other Pt(0) allene

(11) 7: In a typical experiment, potassium *tert*-butoxide (45 mg, 0.401 mmol) and tris(triphenylphosphine)platinum (400 mg, 0.41 mmol) were weighed into an oven-dried Schlenk tube and a magnetic stirring bar was added. After adding 10 mL of THF, the Schlenk tube was sealed with a rubber septum, removed from the drybox, and connected to a nitrogen line. A mixture of three isomeric bromocycloheptatrienes (69.4 mg, 0.4 mmol) was weighed into a vial and 1 mL of THF added. This solution was drawn into a syringe and added dropwise to the solution in the Schlenk tube over 10 min. After being stirred overnight, the solution was filtered through Celite and the Celite washed with 25 mL of ether. The solvent was removed in vacuo, and the residue was triturated with 25 mL of hexane. Filtration of this mixture yielded 7 as a light yellow powder (170 mg, 51%): mp 140–144 °C dec; IR (KBr) 3045 w, 3000 w, 1585 m, 1570 s, 1480 s, 1430 s, 1090 s, 740 s, 700 s, 520 s cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 2.94 (td, $^2J_{PtH}$ = 70.4 Hz, $^3J_{PH}$ = 11 Hz, H1), 4.63 (tdd, $^3J_{PtH}$ = 70.8 Hz, J = 9 Hz, J = 7 Hz), 5.64 (m, 2 H), 6.0 (t, J = 4 Hz, 1 H), 6.24 (m, 1 H), 7.2 (Ph_3P, 30 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 27.7 (dd, $^2J_{P(cis)C}$ = 5.09 Hz, $^2J_{P(trans)C}$ = 44.10 Hz), 114.5 (dd, $^3J_{PC}$ = 5.6 Hz, $^3J_{PC}$ = 9.3 Hz, C3), 118.5, 125.7, 127.7 (d, J = 8.6 Hz, Ph_3P, meta) 129.2 (s, Ph_3P, para), 133.5 (m, Ph_3P, ortho), 136.0 (vd, $^1J_{PC}$ = 41.7 Hz, Ph_3P, ipso), 151.0 (dd, $^2J_{P(cis)C}$ = 10.4 Hz, $^2J_{P(trans)C}$ = 60.98 Hz, C2); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 27.3 (td, $^1J_{PtP}$ = 3170.1 Hz, $^2J_{PP}$ = 33.3 Hz), 31.5 (td, $^1J_{PtP}$ = 3266.7 Hz, $^2J_{PP}$ = 33.3 Hz). Anal. Calcd for $C_{43}H_{36}P_2Pt$: C, 63.74; H, 4.45. Found: C, 63.45; H, 4.46.

8: mp 140–144 °C dec; 82% yield; IR 3045 w, 1480 s, 1435 s, 1385 s, 1090 s, 740 s, 690 s, 515 s cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.02 (td, $^2J_{PtH}$ = 72 Hz, $^3J_{PH}$ = 13.2 Hz, H1), 5.16 (tdd, $^3J_{PtH}$ = 66 Hz, $^4J_{PH}$ = 9 Hz, $^4J_{PH}$ = 4.5 Hz, H3), 6.07 (d, J = 12 Hz), 6.13 (d, J = 12 Hz), 6.32, 6.7 (m), 7.0–7.7 (m, Ph_3P); ^{13}C NMR (25 MHz, $CDCl_3$) δ 26.41 (dd, $^2J_{P(trans)C}$ = 43.9 Hz, $^2J_{P(cis)C}$ = 4.9 Hz, Cl), 113.0 (mc, C2), 124.1, 125.8, 127.5 (b s$_1$, Ph_3P, meta), 128.6, 129.2 (s, Ph_3P, para), 129.9, 130.4, 131.7, 132.1, 134.3 (m, Ph_3P, ortho), 136.8 (Ph_3P, ipso, coupling not observed), 156.1 (dd, $^2J_{P(trans)C}$ = 62.3 Hz, $^2J_{P(cis)C}$ = 9.79 Hz); ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 26.2 (td, $^1J_{PtP}$ = 3134 Hz, $^2J_{PP}$ = 30.1 Hz), 32.2 (td, $^1J_{PtP}$ = 3297 Hz, $^2J_{PP}$ = 30.1 Hz). Anal. Calcd for $C_{47}H_{38}P_2Pt$: C, 65.67; H, 4.46. Found: C, 65.25; H, 4.46.

9: mp 144–150 °C dec; 67% yield; IR (KBr) 3050 w, 2900 w, 1660, 1585 m, 1570 w, 1475 s, 1430 s, 1180 m, 1090 s, 995 m, 810 m, 740 s, 690 s, 500 s, 420 m cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.48 (t, $^2J_{PtH}$ = 70.8 Hz), 5.71 (tdt, $^3J_{PtH}$ = 54.6 Hz, $^4J_{P(trans)H}$ = 8.35 Hz, $^4J_{P(cis)H}$ = $^4J_{HH}$ = 2.8 Hz), 6.41 (d, J = 7.6 Hz, 1 H), 6.67 (td, J = 7.3 Hz, 1.1 Hz), 6.7–7.5 (Ph_3P); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.5 (dd, $^2J_{P(cis)C}$ = 5.43 Hz, $^2J_{P(trans)C}$ = 52.2 Hz, C5), 109.9 (dd, $^3J_{PC}$ = 5.3 Hz, $^3J_{PC}$ = 10 Hz, C7), 124.11, 124.37, 125.96, 126.08, 130.68, 131.4, 134.66, 134.8, 140.03, 140.71 (d, J = 9.1 Hz), 143.97 (d, J = 10.3 Hz), 146.17, 164.36 (dd, $^2J_{P(cis)C}$ = 9.6 Hz, $^2J_{P(trans)C}$ = 62.9 Hz, C2), 127.8 (vt, $^3J_{PC}$ = 9.8 Hz, Ph_3P, meta), 129.24 (s, Ph_3P, para), 129.22 (s, Ph_3P, para), 134.1 (m, Ph_3P, meta), 135.385, 135.94, 136.10, 136.64 (135–136, d, $^1J_{PC}$ = 2.5 Hz, Ph_3P, ipso); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 28.97 (td, $^1J_{PtP}$ = 3208 Hz, $^2J_{PP}$ = 28 Hz), 26.46 (td, $^1J_{PtP}$ = 3145 Hz, $^2J_{PP}$ = 28 Hz). Anal. Calcd for $C_{51}H_{40}P_2Pt_1$: C, 67.33; H, 4.75. Found: C, 66.82; H, 4.48.

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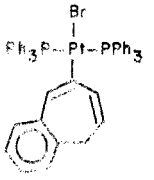
complexes, the probable mechanism for formation of 7–9 is that given in Scheme II. However, the known tendency for Pt(0) to insert into carbon–bromine bonds suggested an insertion–elimination mechanism (Scheme III) as a possible alternative. To evaluate this possibility, the $(Ph_3P)_2Pt$ insertion products **18–20** were synthesized, characterized, and subjected to the reaction conditions. In no case was any reaction observed.



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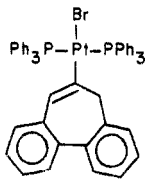

20

In summary, $(Ph_3P)_3Pt$ effectively traps cycloheptatetraenes to give allene complexes, one of which requires at least 17 kcal/mol to convert to its carbene isomer. This is in marked contrast to Fp^+, Rp^+ (Rp = $RuCp(CO)_2$), or $(CO)_5W$ complexes of the parent and in one case (M = Fp^+) the monobenzoannelated ring corresponding to 8, all of which exist solely as carbene complexes. This marked difference between the d^6 and d^{10} metals rests primarily on the availability of a significantly lower lying LUMO in the former.[10]

Acknowledgment. Support for this work by the National Science Foundation is gratefully acknowledged. W.R.W. also acknowledges a fellowship from the Proctor and Gamble Co. We thank the Center for Instructional Research Computing Activities, University of Florida, for a grant of computer time. High-field NMR spectra were obtained on a Nicolet NT-300 spectrometer, operating at a field of 7 T; therefore acknowledgment is made to the Instrument Program, Chemistry Division, National Science Foundation, for financial assistance in the purchase of this instrument.

(19) **18**: tetrakis(triphenylphosphine)platinum (1.07 g, 0.86 mmol) was weighed into a round-bottom flask equipped with a magnetic stirrer and a nitrogen inlet. A mixture of isomeric bromocycloheptatrienes (1.0 g, 5.85 mmol) in 50 mL of benzene was added and the mixture stirred overnight. The solvent was removed in vacuo and the product triturated with 50 mL of ether. The precipitate was filtered and dried in vacuo to give **18**, devoid of the 2- and 3-isomers (0.680 g, 89%): mp 216.0–216.5 °C dec IR (KBr) 3050 w, 3010 w, 1571 w, 1505 m, 1480 m, 1430 s, 1385 m, 1180 m, 1100 s, 1030 m, 1000 m, 750 m, 700 s, 500 s cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 2.23 (td, $^3J_{PtH}$ = 39 Hz, J_{HH} = 7.1 Hz, H7), 4.30 (dt, J = 6.84 Hz, J = 6.0 Hz, 1 H), 5.6 (t, J_{PtH} = 32 Hz, 1 H), 5.64 (s, 2 H), 6.0 (s, 3 H), 7.2 (Ph_3P, 18 H), 7.7 (Ph_3P, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) 80.5 (C7), 115.4, 122.9, 124.58, 127.70 (t, $^3J_{PC}$ = 5.27 Hz, Ph_3P, meta), 130.1 (s, Ph_3P, para), 131.0 (t, $^2J_{PtC}$ = 46 Hz, Ph_3P, ipso), 134.3, 134.45, 135.2 (m, Ph_3P, ortho), 139.4 (Cl); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.34 (t, $^1J_{PtP}$ = 3215 Hz). Anal. Calcd for $C_{43}H_{37}BrP_2Pt$: C, 57.94; H, 4.15. Found: C, 57.76; H, 4.23.

19: mp 218–219 °C dec; 61% yield; IR (KBr) 3065, 3020 w, 1610 w, 1485 s, 1440 s, 1390 s, 1100 s, 750 m, 700 s, 540 s cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.6 (d, $^3J_{HH}$ = 3 Hz, 47), 4.68 (m, 1 H), 5.8 (td, $^3J_{PtH}$ = 38 Hz, J_{HH} = 10 Hz), 6.4–7.1 (m, 5 H), 7.2 (18 H, Ph_3P), 7.7 (12 H, Ph_3P); ^{13}C NMR (25 MHz, CD_2Cl_2) δ 33.3 (C7), 121 (t, $^2J_{PtC}$ = 72 Hz), 124.7, 126.1, 126.2, 126.5, 128.1 (d, $^3J_{PC}$ = 4.9 Hz, Ph_3P, meta), 130.4, 130.5 (s, Ph_3P, para), 131.3 (td, $^2J_{PtC}$ = 28 Hz, $^1J_{PC}$ = 15.9 Hz, Ph_3P, ipso), 134.4, 135.5 (d, $^2J_{PC}$ = 6.1 Hz, Ph_3P, ortho), 139.1, 142.8 (d, $^2J_{PC}$ = 17.1 Hz, C4); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 22.0 (t, $^1J_{PtP}$ = 3189.4 Hz).

20: mp 281–283 °C dec; 86% yield; IR (KBr) 3060 w, 1590 m, 1485 s, 1440 s, 1390 s, 1195 w, 1105 s, 1000 m, 840 m, 755 s, 695 s, 520 s cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 5.50 (t, $^3J_{PtH}$ = 68.4 Hz, 2 H, H7), 6.6 (m), 7.2 (b s, Ph_3P); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.6 (C7), 123.4 (CH), 124.9 (CH), 125.6 (CH), 126.5 (CH), 127.0 (CH), 127.3 (CH), 127.7 (Ph_3P, meta), 128.4, 129.1, 130.0 (Ph_3P, para), 132.1 (t, $^3J_{PC}$ = 7.2 Hz, C2), 135.1 (vt, $^2J_{PC}$ = 6 Hz, Ph_3P, ortho), 136.9, 139.2, 139.6, 139.8, 147.1 (t, $^2J_{PC}$ = 17.9 Hz, C1); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 22.7 (t, $^1J_{PtP}$ = 3190 Hz).

(Fulvalene)dimolybdenum Pentacarbonyl Diphosphine: A Dinuclear Organometallic Zwitterion

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Received September 4, 1985

Summary: Treatment of (η^5:η^5-fulvalene)dimolybdenum hexacarbonyl ($FvMo_2(CO)_6$, **1**) with $P(CH_3)_3$ or $(CH_3)_2PCH_2P(CH_3)_2$ gives the dinuclear zwitterions $FvMo_2(CO)_5L_2$ (**2a,b**) in a reaction that does not proceed via the metal–metal bonded $FvMo_2(CO)_5L$ as an intermediate. Complex **2b** was characterized by X-ray crystallography. The zwitterionic species show reactivity patterns consistent with the charge-localized structure: the negatively charged metal center undergoes attack by electrophiles (**2a,b**), whereas the positively charged center undergoes reduction with one-electron reductants and $LiAlH_4$ (**2a**). When treated with an excess of $P(CH_3)_3$, **2a** and **2b** undergo decomplexation to form $FvMo(CO)_2L_2$ (**12a,b**) in which only one Cp moiety of the Fv ligand is complexed to Mo.

The ligand-induced disproportionation of $[CpMo(CO)_3]_2$ to $[CpMoL_2(CO)_2]^+[CpMo(CO)_3]^-$ (particularly for L = phosphine) has been known for some time.[1] Recently, Tyler and co-workers have studied the mechanism of the photochemically induced disproportionation in detail.[2] We have been interested in the chemistry of carbonyl (η^5:η^5-fulvalene)dimetal (FvM_2) complexes,[3] in which the metals are forced to remain in close proximity, even after the metal–metal bond is broken. We report here the thermal reaction of $FvMo_2(CO)_6$ (**1**) with the strongly donating phosphines $P(CH_3)_3$ and $(CH_3)_2PCH_2P(CH_3)_2$ (dmpm), leading to the first dinuclear organometallic zwitterions $FvMo_2(CO)_5L_2$ (**2a,b**). The reactivity of these complexes, one of which has been structurally characterized, clearly reflects the zwitterionic nature of these systems.

Treatment of **1** with $P(CH_3)_3$ in THF (0 °C, 48 h) gave $FvMo_2(CO)_5[P(CH_3)_3]_2$ (**2a**) in 63% yield.[4] A similar product was obtained with dmpm (**2b**, 45 °C, 4 h, 77%).[4] To our knowledge, these are the first examples of dinuclear, metal-centered organometallic zwitterions. Because of its novelty an X-ray structural characterization was undertaken of **2b**[4] (Figure 1). The Mo–Mo bond has been broken, and the two metal centers are coordinated to the fulvalene ligand in a trans manner. The average Mo1–CO bond length, 1.974 Å, is considerably larger than the av-

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