complexes, each with deuterium incorporated exclusively in the β-position of the ring.[17] The ethyl complex $(C_5Me_5)Ir(\eta^3\text{-allyl})Et$ (**5**), prepared by treatment of $(C_5Me_5)Ir(\eta^3\text{-allyl})Cl$ with EtMgCl,[18] does not rearrange to metallacyclobutane complex **4** under any conditions; this complex cannot be intermediate in the metallacyclobutane formation.

Enolates also add selectively to the central allyl position, producing stable metallacyclobutane complexes epimeric at the metallacycle β-carbon. The reactions of **2-*exo*** and **2-*endo*** with the potassium enolate of propiophenone (THF, −35 °C → room temperature), for example, yield metallacyclobutane stereoisomers **6**[15] and **7**,[15] respectively (Scheme I). By $^1H$ NMR spectroscopy, the crude reaction mixtures reveal no trace of isomeric "leakage" in the addition reaction. Both complexes display the characteristic upfield $^{13}C$ NMR signals for the α-carbons, now diastereotopic due to the chiral center on the addend. Iodinolysis (THF, −78 °C) of complexes **6** and **7** each gives the cyclopropanated organic **8**[19] and $[(C_5Me_5)IrI_2]_2$,[5b] which can be converted back to the starting allyl complex **2-*exo*** in a single step.[6]

Stabilized nucleophiles, in contrast, do not give metallacyclobutane products. The addition of potassium dimethylmalonate to **2-*exo*** proceeds regioselectively to the ethylene ligand, giving neutral alkyl allyl complex **9**.[15,18] The reaction of malonate anion with **2-*endo*** is equally selective but gives only terminal *allyl* addition, affording bis(olefin) complex **10** as an approximately 3:1 mixture of isomers.[15] Iodinolysis of this mixture at low temperature quantitatively produces $[(C_5Me_5)IrI_2]_2$[5b] and the free allylated malonate **11**, identified by comparison to an authentic sample. While the origin of this selectivity is not readily apparent, in the absence of steric effects,[20] this observation suggests that the electrophilicity of the coordinated ethylene may vary considerably with the allyl configuration.[21] The absence of metallacyclobutane formation may reflect a change in the kinetic selectivity for stabilized nucleophiles (due to a "later" transition state) or the rapid reversibility of initial nucleophilic attack. The formation of unstable intermediates and the possibility for interconversion of complexes **9** and **10** are under investigation.

On an empirical basis, the selectivity rules of Davies, Green, and Mingos[2] continue to be remarkably successful in predicting the outcome of nucleophilic additions. Nonetheless, the addition of strong nucleophiles to the $\eta^3$-allyl rather than ethylene ligand in this geometrically unconstrained system clearly violates these rules. Equally importantly, the preference for attack at the $\eta^3$-allyl central carbon rather than the terminal carbon is maintained in this system, despite replacing the strongly donating phosphine with the π-acidic ethylene ligand. Taken together, these results suggest that the coordination geometry of the complex may be more important than the degree of electron richness in determining the regiochemistry of nucleophilic addition to the $\eta^3$-allyl ligand, supporting alternative theoretical interpretations of the regioselectivity issue.[22] These results also suggest that the selectivity for terminal allyl addition observed in the (1-3)-$\eta^3$:(5,6)-$\eta^2$-cycloalkadienyl systems[5] may arise from geometrical constraints that change the relative ordering of the frontier orbitals, render the transition state for metallacyclobutane formation energetically inaccessible, or promote rapid rearrangement of a metallacyclobutane intermediate too strained to be isolated.

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**Supplementary Material Available:** Spectroscopic and analytical data for compounds **4**, **6**, **7**, **9**, and **10** and spectroscopic data for complex **5** (2 pages). Ordering information is given on any current masthead page.

(17) From analysis of both $^1H$ and $^2H$ NMR spectroscopy, on addition of $NaBD_4$, **2-*exo*** yields complex **4-$d_1$** with deuterium incorporated specifically at the position corresponding to the $^1H$ NMR signal at δ 2.80. Complex **2-*endo*** gives **4-$d_1$** with the label exclusively at δ 4.14.

(18) Several closely analogous complexes have been prepared: McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246. The allyl configuration in these complexes has yet to be unambiguously assigned.

(19) Perkins, M. J.; Peynircioglu, N. B.; Smith, B. V. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1025.

(20) From inspection of the X-ray crystal structures of both *exo* and *endo* allyl ethylene complexes[6] and with standard trajectory analysis for the incoming nucleophile, there is no obvious steric argument accounting for the malonate positional selectivity or, in the case of strong nucleophiles, for the kinetic selectivity leading to metallacyclobutane complexes.

(21) The ethylene ligand in **2-*exo*** is fluxional at room temperature, while that in **2-*endo*** is rigid,[6] suggestive of greater backbonding, higher electron density, and lower electrophilicity for the ethylene in the latter complex.

(22) (a) $\eta^3$-Allyl complexes: Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887. (b) $\eta^4$-Diene complexes: Sautet, P.; Eisenstein, O.; Nicholas, K. M. *Organometallics* **1987**, *6*, 1845.

## Inversion of Configuration in Nucleophilic Vinylic Substitutions of (*E*)-β-Alkylvinyliodonium Tetrafluoroborates with Halides

Masahito Ochiai,* Kunio Oshima, and Yukio Masaki

*Gifu Pharmaceutical University*
*5-6-1 Mitahora Higashi, Gifu 502, Japan*

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Nucleophilic substitutions at vinylic carbons of moderately activated olefins usually proceed with predominant retention of configuration thought to proceed via addition–elimination in most cases.[1] Alternatively, highly activated olefins afford products with partial or complete stereoconvergence via a multistep process. Exclusive inversion in nucleophilic vinylic substitutions, however, has not been observed for simple systems.[1c,2] Nucleophilic vinylic substitution generally requires activating substituents at the β-position of vinylic substrates (usually vinyl halides), and nucleophilic substitutions of simple alkylvinylic substrates are very uncommon.[3] We report herein a nucleophilic vinylic substitution of (*E*)-β-alkylvinyliodonium tetrafluoroborates with halides, *which proceeds with exclusive inversion of configuration at room temperature.*

Alkenyl(phenyl)iodonium tetrafluoroborates serve as the highly activated species of alkenyl halides in nucleophilic substitutions, mostly because of the superleaving ability of the phenyliodonio group.[4] However, little is known about the stereochemical course of the substitutions. Substitution of (*E*)-β-alkylvinyliodonium tetrafluoroborates **1a**,**b** with *n*-$Bu_4NX$, which competes with an alkyne-forming elimination, affords alkenyl halides of (*Z*) stereochemistry in completely stereoselective manner (Table I).[5] Treatment of (*E*)-1-decenyliodonium salt **1a** with *n*-$Bu_4NCl$ (10 equiv) in $CH_2Cl_2$ at room temperature for 10 h gave the inverted chloride (*Z*)-**2a**[6] (X = Cl, 83%) and 1-decyne (14%), along with the concomitant formation of iodobenzene. In $CH_3CN$, more than 90% selectivity for the substitution over the elimination was achieved. Substitutions with *n*-$Bu_4NBr$ and *n*-$Bu_4NI$ similarly gave the corresponding (*Z*)-alkenyl halides with complete inversion. On the other hand, *n*-$Bu_4NF$ afforded only 1-decyne. Note that the selectivity for substitution over elimination decreases

(1) (a) Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1. (b) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73. (c) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. (d) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309. (e) Shainyan, B. A. *Usp. Khim.* **1986**, *55*, 942.

(2) (a) Miller, S. I. *Tetrahedron* **1977**, *33*, 1211. (b) Rappoport, Z. *Tetrahedron Lett.* **1978**, 1073.

(3) Stang, P. J.; Datta, A. K. *J. Am. Chem. Soc.* **1989**, *111*, 1358.

(4) For synthesis and reactions of the alkenyliodonium salts, see: (a) Ochiai, M.; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron Lett.* **1985**, *26*, 2351. (b) Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4095. (c) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Goltsev, A. N. *Dokl. Akad. Nauk SSSR*, **1977**, *235*, 591.

(5) Nesmeyanov and his co-workers reported that thermolysis of bis-[(*E*)-1-propenyl(phenyl)iodonium] hexachlorostannate at 85 °C without solvent gave (*Z*)-1-propenyl chloride: Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Leshcheva, I. F. *Dokl. Akad. Nauk SSSR* **1978**, *238*, 1109.

(6) Zweifel, G.; Miller, J. A. *Org. React.* **1984**, *32*, 375.

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**Table I.** Nucleophilic Vinylic Substitutions of (*E*)-Alkenyl(phenyl)iodonium tetrafluoroborates **1** with *n*-$Bu_4NX$[a]

| run no. | substrate | reagent | solvent | reaction time, h | product, % yield[b] alkenyl halide (*Z*:*E* ratio) | 1-alkyne | ratio[c] | PhI |
|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | *n*-$Bu_4NF$ | $CH_3CN$ | 10 | — | 47 | (0:100) | 100 |
| 2 | **1a** | *n*-$Bu_4NCl$ | $CH_2Cl_2$ | 10 | **2a** (X = Cl), 83 (100:0) | 14 | (85:12) | 91 |
| 3 | **1a** | *n*-$Bu_4NCl$ | $CH_3CN$ | 10 | **2a** (X = Cl), 91 (100:0) | 9 | (91:9) | 99 |
| 4 | **1a** | *n*-$Bu_4NBr$ | $CH_3CN$ | 10 | **2a** (X = Br), 95 (100:0) | 5 | (95:5) | 100 |
| 5 | **1a** | *n*-$Bu_4NI$ | $CH_3CN$ | 10 | **2a** (X = I), 88 (100:0) | 2 | (98:2) | 91 |
| 6 | **1b** | *n*-$Bu_4NCl$ | $CH_3CN$ | 1 | **2b** (X = Cl), 86 (100:0) | 14 | (86:14) | 100 |
| 7 | **1b** | *n*-$Bu_4NBr$ | $CH_3CN$ | 10 | **2b** (X = Br), 96 (100:0) | 3 | (97:3) | 100 |
| 8 | **1b** | *n*-$Bu_4NI$ | $CH_3CN$ | 24 | **2b** (X = I), 99 (100:0) | 1 | (99:1) | 100 |
| 9 | **1c** | *n*-$Bu_4NCl$ | $CH_3CN$ | 48 | **2c** (X = Cl), 8 (66:34) | 36 | (18:82) | 64 |
| 10 | **1c** | *n*-$Bu_4NBr$ | $CH_3CN$ | 48 | **2c** (X = Br), 46 (88:12) | 29 | (61:39) | 89 |
| 11 | **1c** | *n*-$Bu_4NI$ | $CH_3CN$ | 48 | **2c** (X = I), 73 (95:5) | 17 | (81:19) | 97 |

[a] Reactions were carried out using 10 equiv of reagents at room temperature. [b] Determined by gas chromatography. [c] Ratios of 1-alkenyl halides to 1-alkynes.

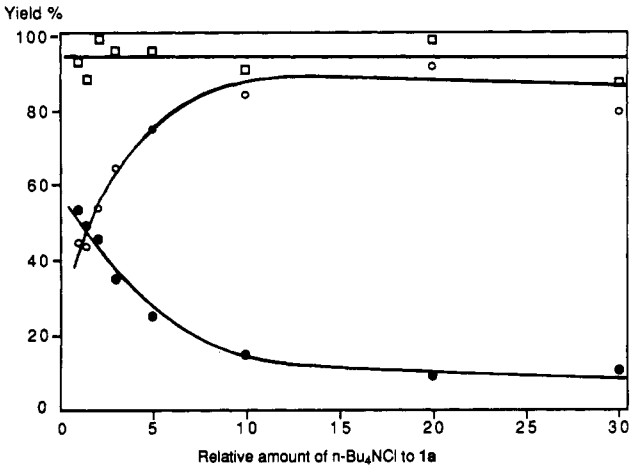



**Figure 1.** The effect of *n*-$Bu_4NCl$ on product distribution of the reaction of **1a** in $CH_2Cl_2$ at 25 °C for 10 h. Symbols are percent yields of (*Z*)-**2a** (X = Cl) (○), 1-decyne (●), and iodobenzene (□).

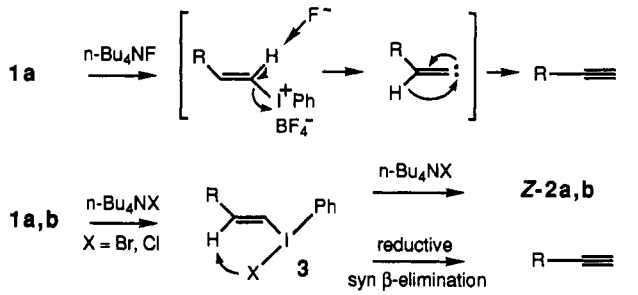
in the order of *n*-$Bu_4NI$ > *n*-$Bu_4NBr$ > *n*-$Bu_4NCl$ ≫ *n*-$Bu_4NF$, reflecting the decreasing softness of halide ions.


**a**: R = n-$C_8H_{17}$; **b**: R = $Ph(CH_2)_3$; **c**: R = Ph

Reaction of β-phenylvinyliodonium salt **1c**, however, was accompanied by formation of retention products to some extent: thus, *n*-$Bu_4NCl$ gave a 66:34 mixture of (*Z*)- and (*E*)-**2c** (X = Cl) in low yield and phenylacetylene as the major product. Decreased amounts of retention products were obtained in the reaction with *n*-$Bu_4NBr$ and *n*-$Bu_4NI$. Again, the selectivity for inversion to retention decreases in the order of *n*-$Bu_4NI$ > *n*-$Bu_4NBr$ > *n*-$Bu_4NCl$. The formation of some retained products from **1c** may arise from an intervention of a vinylidenephenonium ion intermediate, generated by neighboring group participation.[7] Reaction of (*Z*)-1-decenyl(phenyl)iodonium perchlorate with *n*-$Bu_4NCl$ in $CH_2Cl_2$ at 0 °C for 30 min exclusively undergoes elimination to give 1-decyne quantitatively.

In marked contrast, complete retention of stereochemistry was found in substitutions of **1** using a combination of cuprous halides (10 equiv) and potassium halides (10 equiv) in $CH_2Cl_2$ at room temperature in the dark [product (yield)]: (*E*)-**2a** (X = Cl (94%) and Br (91%)), (*E*)-**2b** (X = Cl (70%) and Br (92%)), and (*E*)-**2c** (X = Cl (77%) and Br (80%)).

**Scheme I**




As shown in Figure 1, relative amounts of *n*-$Bu_4NCl$ to **1a** play an essential role in determining the reaction course, that is, substitution and elimination. Surprisingly, primary kinetic deuterium isotope effects and the observed deuterium content of the product 1-decyne in the reaction of α- and β-deuterated **1a** with *n*-$Bu_4NCl$ (2 equiv) in $CH_2Cl_2$ clearly indicate that 1-decyne was predominantly produced as the result of syn β-elimination, and generation of an alkylidenecarbene by α-elimination, which was reported in the reaction of **1a** with triethylamine,[8] was not involved.[9] α-Elimination generating the alkylidenecarbene, however, was found to occur in the reaction with *n*-$Bu_4NF$ (Scheme I).[10]

Addition–elimination pathways are not compatible with exclusive inversion of configuration in the reaction of **1a,b** with *n*-$Bu_4NX$.[11] Ion pairs leading to predominant inversion were suggested in the solvolysis of vinyl triflates,[12] but there are no "primary" vinyl cations known.[13] Direct $S_N2$ displacement at vinylic carbon atoms which predicts inversion of configuration has been shown to be energetically more difficult than that at $sp^3$ carbon atoms.[14]

(7) In the solvolyses of β-arylvinyl triflates, neighboring phenyl participations have been reported: Stang, P. J.; Dueber, T. E. *J. Am. Chem. Soc.* **1977**, *99*, 2602. However, a referee had mentioned that these systems which were studied in 97% TFE with an α-Me substituent are not necessarily good models for the present unsubstituted system. He suggests that a contribution from the "common" retentive bimolecular vinylic substitution accounts for the formation of the retained product.

(8) Ochiai, M.; Takaoka, Y.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 6565.

(9) No loss of deuterium content in the reaction of α-deuterated **1a** (97% D) with 2 equiv of *n*-$Bu_4NCl$ ($CH_2Cl_2$, 25 °C, 10 h) was observed, and 1-decyne-*1-d* and α-deuterated (*Z*)-**2a** (X = Cl) were obtained in 37% and 62% yields, respectively. However, reaction of β-deuterated **1a** (93% D) gave an only 18% yield of 1-decyne-*1-d* (7% D) and an 80% yield of β-deuterated (*Z*)-**2a** (X = Cl, 95% D). These deuterium contents were determined by GC-MS.

(10) Reaction of α-deuterated **1a** (97% D) with 1 equiv of *n*-$Bu_4NF$ ($CH_2Cl_2$, 25 °C, 10 h) afforded an 86% yield of 1-decyne (0% D). On the other hand, the reaction of β-deuterated **1a** (93% D) gave a 76% yield of 1-decyne-*1-d* (95% D).

(11) Furthermore, elimination–addition routes through the formation of terminal alkynes are not consistent with the experimental result that 1-decyne was recovered in the reaction with *n*-$Bu_4NCl$ in the presence of HCl ($CH_3CN$, 25 °C, 10 h).

(12) Summerville, R. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 3629.

(13) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press, New York, 1979.

(14) (a) Kelsey, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1953. (b) Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273. (c) Bunnett, J. F. *Q. Rev.* **1958**, *12*, 1.

A mechanism shown in Scheme I involves a rapid ligand exchange of **1** with halides and thereby formation of vinyliodonium halides **3** as intermediates. It was established by $^1$H NMR that **3** (R = $n$-$C_8H_{17}$, X = Cl) is produced instantaneously by the addition of **1a** to a solution of $n$-$Bu_4NCl$ in $CDCl_3$ at room temperature.[15,16] Furthermore, this compound **3** in $CH_2Cl_2$ at room temperature decomposed to a 45:55 mixture of (*Z*)-**2a** (X = Cl) and 1-decyne quantitatively. Attack of another halide to **3** will produce (*Z*)-**2**, although the mechanism is unknown. Alternatively, intramolecular cis-$\beta$-proton abstraction[9] by the ligand X of **3** gives 1-alkynes. Thus, the relative ratios of the substitution to the alkyne-forming reaction depend on the concentration of halide ions, which is compatible with the results shown in Figure 1.

**Acknowledgment.** This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 02247101 from the Ministry of Education, Science and Culture, Japan, and by Takeda Science Foundation.

(15) The authentic **3** (R = $n$-$C_8H_{17}$, X = Cl) was prepared quantitatively by the reaction of **1a** with NaCl.

(16) On the other hand, **1a** did not undergo the ligand exchange with fluoride ion. This fact could be interpreted by the hard and soft acids and bases principle and may be the reason for the preferential $\alpha$-elimination of **1a** with $n$-$Bu_4NF$.

## Small-Ring Organometallic Systems. Ring Strain and Quantum Yields of Formation in CpMn(CO)($\eta^2$-P-P) Complexes

Amy A. Sorensen and Gilbert K. Yang*

*Department of Chemistry*
*University of Southern California*
*Los Angeles, California 90089-0744*

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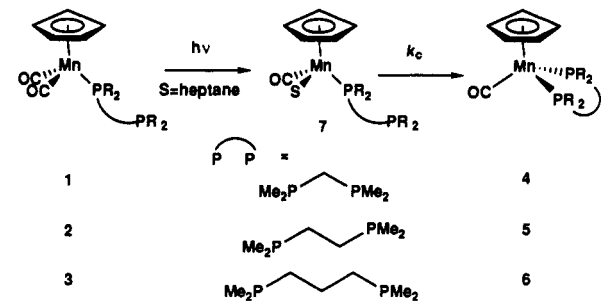
Four-, five-, and six-membered rings abound in organometallic chemistry as proposed catalytic and reactive intermediates and as stable complexes. In light of their role as intermediates in olefin metathesis reactions, four-membered rings are of particular interest. Marks[1] and Puddephatt[2] respectively have determined the strain in thoracyclobutanes and platinacyclobutanes to be 16 and 10–13 kcal/mol while a study of Whitesides[3] suggests that the strain in platinacyclobutanes is less than 5 kcal/mol. From the heat of norbornadiene substitution from (NBD)$Mo(CO)_4$ by bidentate phosphine ligands, Hoff[4] has determined ring strain in four-membered rings containing the P–Mo–P moiety to be 8 kcal/mol. Although it is clear that there is some strain in these systems, the magnitude of the strain is still in some dispute. Studies on classical coordination complexes reveal a dependence of ring strain on chelate ring size.[5] None of these studies have addressed the strain in four-membered metallacycles containing first-row transition elements. We now report the determination of the strain in four-membered rings containing Mn and P atoms by measurement of the enthalpy of cyclization as a function of ring size. The determination of the quantum yield for the ring-closure reactions is also reported.

The reaction of photochemically generated $CpMn(CO)_2THF$ with a roughly 2-fold excess of the appropriate bis(dimethylphosphino)alkane ligand dmpm, dmpe, or dmpp (P–P) gives the corresponding $CpMn(CO)_2(\eta^1$-P–P) complex (**1**, **2**, **3**) in ~70% yield.[6] Only small amounts of the dinuclear $(CpMn(CO)_2)_2(\mu$-P–P) complexes are formed under these conditions. Recrystallization of the crude $\eta^1$-**1** and $\eta^1$-**2** complexes from hexanes removed the dinuclear impurity. The $\eta^1$-**3** complex was difficult to crystallize and was purified by air-free column chromatography (silica-60/hexanes/THF (100:1)). In benzene-$d_6$ solution at room temperature, the $\eta^1$ complexes did not undergo thermal CO loss or ring closure.

Scheme I




Photolysis of the $\eta^1$-bis(dimethylphosphino)alkane complexes **1**, **2**, or **3** with a medium-pressure Hg lamp in heptane solution results in CO dissociation and ring closure to form the corresponding four-, five-, and six-membered rings (**4**, **5**, **6**) in quantitative yield.[7] Photolysis of $\eta^1$-**1**, -**2**, or -**3** in heptane solution under 600 Torr of CO leads only to the cyclized products with no evidence for loss of the phosphine ligand. This result is in agreement with CO loss as the only significant photochemical step.[8] Complex **4** has been previously reported by King and RaghuVeer.[9] The quantum yields at 337.1 nm for the cyclization reactions were directly determined to be 0.62 and 0.60 for $\eta^1$-**1** and $\eta^1$-**2**, respectively.[10] The quantum yield for the ring closure

(1) Bruno, J. W.; Marks, T. J.; Morss, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824–6832.

(2) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149–194.

(3) Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948–949.

(4) Mukerjee, S. L.; Nolan, S. P.; Hoff, C. D.; Lopez de la Vega, R. *Inorg. Chem.* **1988**, *27*, 81–85.

(5) (a) Hancock, R. D.; Wade, P. W.; Ngwenya, M. P.; de Sousa, A. S.; Damu, K. V. *Inorg. Chem.* **1990**, *29*, 1968–1974. (b) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875–1914. (c) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1975; Vol. 2.

(6) Data for **1**: $^1$H NMR (benzene-$d_6$) $\delta$ 4.17 (d, 5 H, $C_5H_5$, $J_{P-H}$ = 2.0 Hz), 1.40 (dd, 2 H, $CH_2$, $J_{P-H}$ = 2.2, 8.1 Hz), 1.15 (d, 6 H, MnP$Me_2$, $J_{P-H}$ = 8.3 Hz), 0.74 (d, 6 H, free P$Me_2$, $J_{P-H}$ = 3.6 Hz). $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 81.27 (s, $C_5H_5$), 39.54 (dd, $CH_2$, $J_{P-C}$ = 30.8, 20.7 Hz), 20.76 (dd, MnP$Me_2$, $J_{P-C}$ = 27.7, 7.6 Hz), 16.38 (dd, free P$Me_2$, $J_{P-C}$ = 14.9, 5.9 Hz). $^{31}$P NMR (benzene-$d_6$) $\delta$ 56.7 (br, Mn*P*), -57.0 (d, free *P*, $J_{P-P}$ = 40.9 Hz). IR (THF) $\nu_{CO}$ 1927, 1861 cm$^{-1}$. Anal. Calcd for $C_{11}H_{19}OMnP_2$: C, 46.17; H, 6.13. Found: C, 46.46, H, 6.23. Data for **2**: $^1$H NMR (benzene-$d_6$) $\delta$ 4.08 (d, 5 H, $C_5H_5$, $J_{P-H}$ = 1.9 Hz), 1.35 (m, 4 H, $CH_2CH_2$), 0.93 (d, 6 H, MnP$Me_2$, $J_{P-H}$ = 8.3 Hz), 0.81 (d, 6 H, free P$Me_2$, $J_{P-H}$ = 2.7 Hz). $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 81.0 (s, $C_5H_5$), 31.91 (dd, MnP$CH_2$, $J_{P-C}$ = 22.4, 13.1 Hz), 26.14 (dd, MnPCH$_2$CH$_2$, $J_{P-C}$ = 13.7, 2.0 Hz), 19.00 (d, MnP$Me_2$, $J_{P-C}$ = 26.5 Hz), 13.79 (d, free P$Me_2$, $J_{P-C}$ = 15.4 Hz). $^{31}$P NMR (benzene-$d_6$) $\delta$ 59.8 (br, Mn*P*), -47.1 (d, free *P*, $J_{P-P}$ = 28.1 Hz). IR (THF) $\nu_{CO}$ 1927, 1861 cm$^{-1}$. Data for **3**: $^1$H NMR (benzene-$d_6$) $\delta$ 4.12 (d, 5 H, $C_5H_5$, $J_{P-H}$ = 2.0 Hz), 1.4 (m, 4 H), 1.1 (m, 2 H), 0.95 (d, 6 H, MnP$Me_2$, $J_{P-H}$ = 8.5 Hz), 0.84 (d, 6 H, free P$Me_2$, $J_{P-H}$ = 2.6 Hz). $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 81.01 (s, $C_5H_5$), 37.29 (dd, MnP$CH_2$, $J_{P-C}$ = 24.1, 10.8 Hz), 34.10 (t, MnPCH$_2$CH$_2$, $J_{P-C}$ = 11.7 Hz), 20.86 (dd, MnPCH$_2$CH$_2$CH$_2$, $J_{P-C}$ = 14.5, 0.7 Hz), 19.18 (d, MnP$Me_2$, $J_{P-C}$ = 26.7 Hz), 14.04 (d, free P$Me_2$, $J_{P-C}$ = 14.6 Hz). $^{31}$P NMR (benzene-$d_6$) $\delta$ 56.0 (br, Mn*P*), -53.6 (s, free *P*). IR (THF) $\nu_{CO}$ 1926, 1861 cm$^{-1}$.

(7) Data for **4**: $^1$H NMR (benzene-$d_6$) $\delta$ 4.08 (t, 5 H, $C_5H_5$, $J_{P-H}$ = 2.0 Hz), 2.8 (m, 2 H, CH$^a$CH$^b$), 1.29 (t, 6 H, $Me^a$, $J_{P-H}$ = 4.6 Hz), 1.08 (t, 6 H, $Me^b$, $J_{P-H}$ = 4.4 Hz). $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 75.82 (s, $C_5H_5$), 54.95 (t, $CH_2$, $J_{P-C}$ = 16.7 Hz), 22.45 (t, $Me^a$, $J_{P-C}$ = 13.7 Hz), 21.51 (t, $Me^b$, $J_{P-C}$ = 4.3 Hz). $^{31}$P NMR (benzene-$d_6$) $\delta$ 34.78 (br). IR (heptane) $\nu_{CO}$ 1844 cm$^{-1}$. Data for **5**: $^1$H NMR (benzene-$d_6$) $\delta$ 3.98 (t, 5 H, $C_5H_5$, $J_{P-H}$ = 2.1 Hz), 1.34 (m, 6 H, $Me^a$), 1.22 (m, 2 H, CH$^a$CH$^b$), 1.08 (m, 2 H, CH$^a$CH$^b$), 0.88 (m, 6 H, $Me^b$). $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 76.53 (s, $C_5H_5$), 31.55 (m, $CH_2$), 22.16 (m, $Me^a$), 20.87 (m, $Me^b$). $^{31}$P NMR (benzene-$d_6$) $\delta$ 90.6 (br). IR (THF) $\nu_{CO}$ 1827 cm$^{-1}$. Anal. Calcd for $C_{12}H_{21}OMnP_2$: C, 48.34, H, 7.10. Found: C, 48.41, H, 6.89. Data for **6**: $^1$H NMR (benzene-$d_6$) $\delta$ 3.98 (t, 5 H, $C_5H_5$, $J_{P-H}$ = 2.1 Hz), 1.7 (m, 2 H, PCH$_2$CH$_2$), 1.35 (m, 4 H, PC$H_2$), 1.14 (t, 6 H, P$Me^a_2$, $J_{P-H}$ = 4.1 Hz), 0.93 (t, 6 H, P$Me^b_2$), $J_{P-H}$ = 3.7 Hz). $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 77.79 (s, $C_5H_5$) 32.57 (dd, $CH_2$, $J_{P-C}$ = 14.6, 15.5 Hz), 24.72 (dd, $CH_2$, $J_{P-C}$ = 13.2, 14.1 Hz), 20.84 (dd, $Me^a$, $J_{P-C}$ = 5.6, 6.3 Hz), 20.15 (t, $Me^b$, $J_{P-C}$ = 1.3 Hz). $^{31}$P NMR (benzene-$d_6$) $\delta$ 55.9 (br). IR (THF) $\nu_{CO}$ 1822 cm$^{-1}$. Anal. Calcd for $C_{13}H_{23}OMnP_2$: C, 50.03, H, 7.43. Found: C, 50.35, H, 7.50.

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