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Interaction of Trialkylaluminum Reagents with Organotransition-Metal π-Complexes: One-Step, High-Yield Ethylation of [(Arene)$_2$Fe]$^{2+}$ Cations

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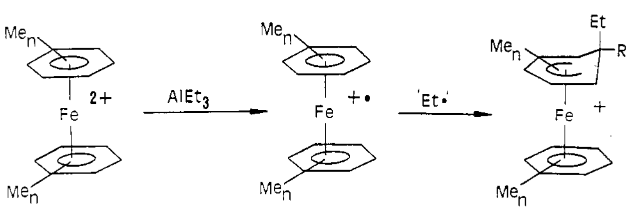
Summary: Triethylaluminum has been utilized to ethylate the series [(arene)$_2$Fe](PF$_6$)$_2$ (arene = benzene (**1a**), mesitylene (**1b**), pentamethylbenzene (**1c**), and hexamethylbenzene (**1d**)) in one facile, high-yield step. Monocationic cyclohexadienyl complexes were the only isolable products, and yields improved as the degree of substitution of the arene ring increased. To our knowledge the ethylation of **1d** represents the first example of direct, high-yield alkylation at an alkylated arene ring position and therefore offers a convenient opening to subsequent synthesis of useful bifunctionalized cyclohexadiene complexes. X-ray crystal structures are reported for the cyclohexadienyl complexes derived from **1b** and **1d**.

Carbon–carbon bond formation via direct addition of carbanionic moieties to transition-metal-coordinated arenes offers a versatile and well-established[2–6] method of arene functionalization and is the key first step in conversion of arenes to synthetically useful bifunctionalized cyclohexadienes. However, few systems have been subjected to double nucleophilic addition with apparently only one example of direct double carbanion addition having thus far been reported.[7] Dicationic moieties would seem to be suitable substrates for formation of bifunctionalized cyclohexadienes, since double anion addition would yield neutral products. Activity has therefore tended to concentrate upon such moieties. Several systems have been studied in this context: [(arene)$_2$Fe]$^{2+}$;[8–10] [(C$_6$H$_6$)(C$_5$Me$_5$)M]$^{2+}$ (M = Rh, Ir);[11] [(C$_6$H$_6$)(C$_6$Me$_6$)Ru]$^{2+}$;[11] and [(C$_6$H$_6$)(C$_5$H$_5$)Co]$^{2+}$.[7] The isoelectronic [(arene)Mn(CO)$_3$]$^+$ series of monoactions has been bifunctionalized in a similar manner, directly with hydride[12] and indirectly via the corresponding [(cyclohexadienyl)Mn(CO)$_2$(NO)]$^+$ cation.[13]

Scheme I



1a–d 3a–d 2a–d

With regards to ease and cost of synthesis the [(arene)$_2$Fe]$^{2+}$ series of cations offer the greatest promise as suitable substrates for further activity, especially as they are even reactive with weak nucleophiles.[14] Unfortunately a major drawback to their use is that they cannot be directly converted to the corresponding [(cyclohexadienyl)(arene)Fe]$^+$ cations via C–C bond formation using conventional (i.e. Grignard, organocuprate, organolithium) carbanion sources.[15] In this communication we report the results of an investigation into the reactivity of [(arene)$_2$Fe]$^{2+}$ cations (arene = benzene (**1a**), mesitylene (**1b**), pentamethylbenzene (**1c**), and hexamethylbenzene (**1d**)) with AlEt$_3$,[16] a reagent which recently has been proven effective for moderate yield ethylation of [(arene)Mn(CO)$_3$]$^+$ cations.[17]

Two observations stand out from the results of our investigation: first, single ethylation of one arene ring producing the monocationic cyclohexadienyl products **2a–d** was the major reaction even in the presence of excess triethylaluminum; second, yields of ethylation products unexpectedly[18] increased with substitution of the arene ring, **2d** being isolated in recrystallized yields of greater than 90%.[19] The alkylating capability of AlEt$_3$ therefore complements that of the more conventional reagents which are not effective at direct alkylation of **1a–d** and would not normally be expected to add in a facile manner to a substituted ring carbon atom (as happens in formation of **2d**).[18] This reactivity can be attributed to the existence of ET processes in these reactions (see below).

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(1) (a) Dalhousie University. (b) Saint Mary's University.

(2) Davies, S. G.; Green, M. L. H., Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.

(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 921–940.

(4) Astruc, D. *Tetrahedron* **1983**, *39*, 4027.

(5) Davies, S. G. *Organotransition Metal Chemistry*: *Applications to Organic Synthesis*, Pergamon: Oxford, 1982.

(6) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957.

(7) Yee-Hing, L.; Wilson, T.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1981**, *216*, 97.

(8) Madonik, A. M.; Mandon, D.; Michaud, P.; Lapinte, C.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 3381.

(9) Mandon, D.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1986**, *108*, 1320.

(10) Mandon, D.; Astruc, D. *J. Organomet. Chem.* **1986**, *307*, C27.

(11) Grundy, S. L.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1982**, 379.

(12) Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638.

(13) Chung, Y. K.; Choi, H. S.; Sweigart, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 4245.

(14) [(C$_6$H$_6$)$_2$Fe]$^{2+}$ is attacked by trialkyl phosphites: Sweigart, D. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1159.

(15) Astruc et al. have reported that for [(arene)$_2$Fe]$^{2+}$ salts, except **1b**, carbanion sources fail to react via carbon–carbon bond formation (ref 8). **1b** reacts readily with a variety of carbanionic nucleophiles (Helling, J. F.; Cash, G. G. *J. Organomet. Chem.* **1974**, *73*, C10. Helling, J. F.; Braitsch, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 7207).

(16) In a typical reaction 1.00 g of the bis(arene) salt was suspended in 100 mL of 1,2-dichloroethane to which was added 4 equiv of AlEt$_3$ (in an inert atmosphere glovebox). After the resulting solution was stirred for 18 h the flask was cooled to 0 °C and quenched with ice water. The mixture was then filtered and the ClCH$_2$CH$_2$Cl phase was separated and concentrated under reduced pressure to give an orange or red solid. After the mixture was washed with distilled hexanes, the solid was recrystallized via partial evaporation of an acetone/water or acetonitrile/water mixture.

(17) Reaction of [(arene)Mn(CO)$_3$]$^+$ cations with AlR$_3$ (R = Me, Et) gave minor dimerization products in addition to the expected alkylation products (Gaudet, M. V.; Hanson, A. W.; White, P. S.; Zaworotko, M. J. *Organometallics*, accepted for publication).

(18) A survey of the literature revealed only one example of carbanion addition to a substituted ring position of a coordinated arene, and yields were small as a result of a competing reaction (Munro, G. A. M.; Pauson, P. L. *Isr. J. Chem.* **1976/1977**, *15*, 258).

(19) Crude yields (PF$_6^-$ salts): for **2a**, 0.22 g (28%) ([PEt$_4$]$^+$ was also isolated); **2b**, 0.62 g (77%) ([(C$_6$H$_3$Me$_3$)(*exo*-CH$_2$CH$_2$ClC$_6$H$_3$Me$_3$)Fe]PF$_6$ was a minor product in this reaction), **2c**, 0.66 g (80%); and **2d**, 0.77 g (93%). A pure sample of **2b** can be obtained, however, if the reaction is carried out by using the salt **1b**$^{2+}$(I$^-$)$_2$ and benzene as a solvent. Extraction of the reaction mixture with H$_2$O following heating to 50 °C for 24 h, and precipitation with NH$_4$PF$_6$(aq) yields the pure complex **2b**.

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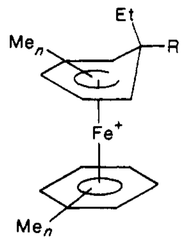

2a: n = 0; R = H
b: n = 3, 1,3,5-Me$_3$; R = H
c: n = 5; R = H
d: n = 5; R = Me

Compounds **2a–d** were isolated as their PF$_6^-$ salts and characterized via ^{1}H and ^{13}C NMR and elemental analysis.[20] Additionally, the PF$_6^-$ salts of **2b** and **2d** were characterized by single-crystal X-ray diffraction.[21] Views of **2b** and **2d** are presented in Figure 1. The cations represent the expected products of exo addition and are the first examples of crystallographically characterized mixed cyclohexadienyl–arene complexes. Although the cations are similar, **2d** exhibits several manifestations of steric strain.[22]

The observations are consistent with an ET/radical coupling process rather than a direct nucleophilic addition. That a second ethylation step does not occur may then be attributed to the difference in reduction potential between **1a–d**[23] and **2a–d**.[24] A plausible mechanism is that AlEt$_3$ acts initially as a one-electron reducing agent[25] and alkylation subsequently occurs via radical coupling of the reactive 19-electron [(arene)$_2$Fe]$^+$ cation and an ethyl-containing radical (see Scheme I). This assertion is borne out by several observations both in this study and in our recent investigations into the reactivity of [(arene)(C$_5$H$_5$)Fe]$^+$, [(arene)Mn(CO)$_3$]$^+$, and [(C$_5$H$_5$)$_2$Co]$^+$ cations with AlEt$_3$.[26] For example, immediately upon addition of AlEt$_3$ to the reaction flask, a deep purple solution was observed, indicative of the known 19-electron monocationic complexes **3a–d**.[27] Furthermore, if the reactions were carried out in dichloromethane, a mixture of products was isolated from **1b**. The chloromethyl cyclohexadienyl **2e** was isolated as a major product along with **2b** (the CH$_2$CH$_2$Cl analogue **2f** was isolated as a minor product when ClCH$_2$CH$_2$Cl was used as a solvent[20]). Presumably, the organometallic radical **3b** reacts with the solvent to give the chloroalkyl products.[28] Finally, in reactions conducted using AlMe$_3$ as the alkyl source, we have so far isolated reduction rather than alkylation products (cf. RLi).[29]

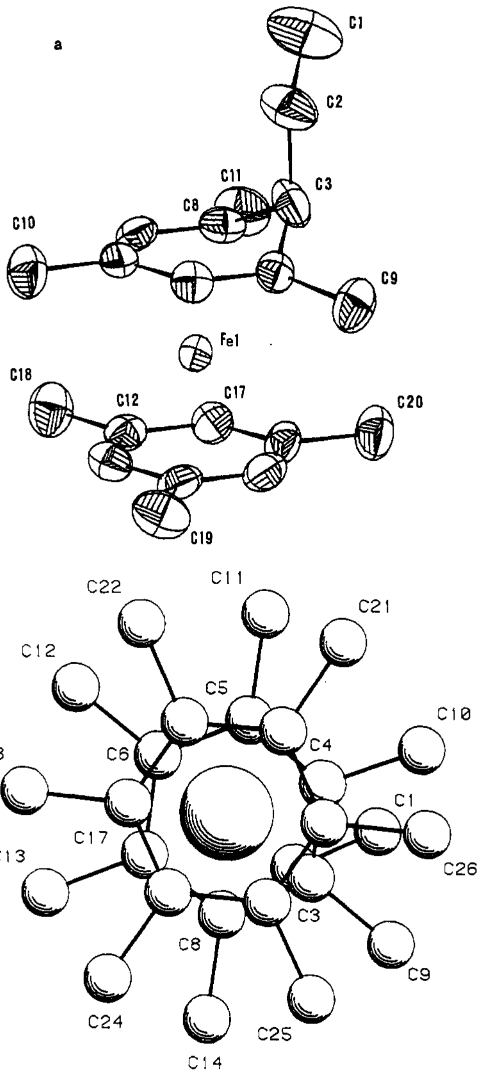

Figure 1. (a) Perspective view of **2b** and (b) overhead view of **2d** (hydrogen atoms have been omitted for clarity). Fe–C(arene), Å: **2b**, 2.081–2.130, average 2.11 (2); **2d**, 2.138–2.179, average 2.16 (1). Fe–C(cyclohexadienyl), Å: **2b**, 2.056–2.161, average 2.10 (4); **2d**, 2.082–2.179, average 2.12 (4).

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[20] [(C$_6$H$_6$)(EtC$_6$H$_6$)Fe]PF$_6$ (**2aPF$_6$**): ^{1}H NMR ((CD$_3$)$_2$CO) δ 6.95 (t, 1 H), 6.43 (s, 6 H), 4.92 (t, 2 H), 3.93 (t, 2 H), 0.39 (m, 5 H); ^{13}C NMR δ 91.5 d, 85.7 d, 84.6 d, 48.9 d, 37.4 d, 34.5 t, 6.2 q. [(C$_6$H$_3$Me$_3$)(EtC$_6$H$_3$Me$_3$)Fe]PF$_6$ (**2bPF$_6$**): ^{1}H NMR (CDCl$_3$) δ 5.20 (s, 3 H), 3.84 (s, 2 H), 2.55 (s, 3 H), 2.29 (s, 9 H), 1.53 (s, 6 H), 0.44 (m, 5 H); ^{13}C NMR (CDCl$_3$) δ 102.0 s, 94.9 s, 92.5 d, 84.0 d, 63.0 s, 49.0 d, 29.8 t, 23.3 q, 18.7 q, 11.3 q, 5.3 q. [(C$_6$HMe$_5$)(EtC$_6$HMe$_5$)Fe]PF$_6$ (**2cPF$_6$**): ^{1}H NMR (CDCl$_3$) δ 4.92 (s, 1 H), 2.36 (s, 3 H), 2.30 (s, 6 H), 2.15 (s, 6 H), 1.81 (s, 3 H), 1.71 (s, 6 H), 1.36 (s, 6 H), 0.24 (m, 5 H); ^{13}C NMR (CDCl$_3$) δ 102.1 s, 100.6 s, 97.6 s, 92.0 d, 91.8 s, 90.2 s, 56.5 s, 53.3 d, 29.8 t, 20.8 q, 18.3 q, 15.0 q, 14.4 q, 14.2 q, 14.1 q, 13.9 q. [(C$_6$Me$_6$)(EtC$_6$Me$_6$)Fe]PF$_6$ (**2dPF$_6$**): ^{1}H NMR ((CD$_3$)$_2$CO) δ 2.51 (s, 3 H), 2.30 (s, 18 H), 1.88 (s, 6 H), 1.48 (s, 3 H), 1.31 (s, 6 H), 0.27 (m, 5 H); ^{13}C NMR ((CD$_3$)$_2$CO) δ 100.8 s, 92.6 s, 56.8 s, 45.4 s, 42.3 s, 37.8 t, 21.8 q, 15.9 q, 15.5 q, 14.5 q, 14.2 q, 9.0 q. Satisfactory analyses were obtained for **2b–d** if water of solvation is taken into account. Analysis could not be obtained for **2a** since isolation of a pure sample was not possible (see ref 19).

[21] [(η^6-C$_6$H$_3$Me$_3$)(η^5-*exo*-EtC$_6$H$_3$Me$_3$)Fe]PF$_6$ (**2b**) crystallizes in the orthorhombic space group $P2_12_12_1$ (Z = 4) with a = 8.880 (2), b = 15.243 (3), and c = 15.457 (3) Å, V = 2092.2 Å^3, D_{calcd} = 1.455 g cm^{-3}, and R = 0.039 (R_w = 0.040) for 1476 unique reflections with $I \geq 2\sigma(I)$ and 306 least-squares parameters; [(η^6-C$_6$Me$_6$)(η^5-*exo*-EtC$_6$Me$_6$)Fe]PF$_6$ (**2d**) crystallizes in the monoclinic space group $C2/c$ (Z = 8) with a = 34.295 (5), b = 10.332 (2), and c = 16.262 (3) Å, β = 115.604 (13)°, V = 5196.4 Å^3, D_{calcd} = 1.417 g cm^{-3}, and R = 0.056 (R_w = 0.058) for 2038 unique reflections with $I \geq 2\sigma(I)$ and 393 least-squares parameters.

[22] The methyl carbon atoms of the η^6-ring all point away from the metal at an average distance of 0.10 Å; the ring carbon atoms are staggered (Figure 1b); the Fe–C bond lengths are significantly longer than those in [(C$_5$H$_5$)Fe(arene)]$^+$ complexes (Hamon, J. R.; Saillard, J. Y.; Le Beuze, A.; McGlinchey, M. J.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 7549. Dubois, R. H.; Zaworotko, M. J.; White, P. S. *J. Organomet. Chem.*, submitted for publication); the planarity of both rings is reduced.

[23] The reduction potential of **2d** has been measured as −0.5 V, and the other salts are assumed to be approximately equal (Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1982**, *104*, 3755).

[24] Even though cations like **2a–d** have not been investigated electrochemically [(C$_5$H$_5$)Fe(arene)]$^+$ cations have reduction potentials in the range −1.37 to −1.67 V vs SCE. (Astruc, D. *Acc. of Chem. Res.* **1986**, *19*, 377).

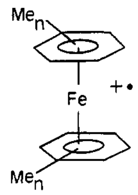
[25] AlEt$_3$ has been shown to react via ET mechanisms with organic substrates: Ashby, E. C.; Goel, A. B. *J. Organomet. Chem.* **1981**, *221*, C15.

[26] The former class of salt is unreactive ($E°$ ≈ −1.5 V) whereas the latter two have reduction potentials of ∼−0.9 V (Dessy, R. E.; Stary, F. E.; King, R. B.; Waldrop, M. J. *J. Am. Chem. Soc.* **1987**, *88*, 471. Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2632) and readily undergo ethylation.

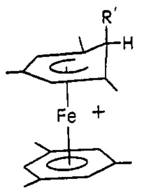
[27] Michaud, P.; Mariot, J. P.; Varret, F.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1982**, 1383.

[28] Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1987**, *26*, 253.

[29] Reaction of **1d** with AlMe$_3$ in CH$_2$Cl$_2$ initially yields a purple paramagnetic complex believed to be the corresponding 19-electron species isolated by Astruc et al. (ref 27), which reacts in situ with CH$_2$Cl$_2$ to yield the chloromethyl analogue of **2d**.



3a: $n = 0$
b: $n = 3$ (1,3,5)
c: $n = 5$
d: $n = 6$



2e: R′ = CH_2Cl
f: R′ = CH_2CH_2Cl

In summary, this paper details a one-step, high-yield method of carbon–carbon bond formation utilizing the readily accessible $[(arene)_2Fe]^{2+}$ series of dications and $AlEt_3$. $AlEt_3$ has therefore been shown to be an effective complement to more conventional carbanionic sources, presumably because of its tendency to engage in ET reactions with organotransition-metal substrates. We are extending this work in our laboratory by focusing upon other trialkylaluminum reagents and further functionalization of **2a–d**.[30]

Acknowledgment. We are indebted to NSERC (M. J.Z., T.S.C.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (M.J.Z.), for financial support and to Dr. Don Hooper of the Atlantic Regional Magnetic Resonance Centre (ARMRC) for recording ^{13}C NMR spectra.

Registry No. **1a**, 11108-19-3; **1b**, 31666-55-4; **1b**$^+$ $(I^-)_2$, 12148-60-6; **1c**, 59688-09-4; **1d**, 53382-63-1; **2a** PF_6, 117340-92-8; **2b** PF_6, 117340-94-0; **2c** PF_6, 117340-96-2; **2d** PF_6, 117340-98-4; **2f** PF_6, 117341-00-1; **3d**, 53382-60-8; $AlEt_3$, 97-93-8; $AlMe_3$, 75-24-1; $[(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}exo\text{-}CH_2Cl_6Me_6)Fe]^+$, 117341-01-2.

Supplementary Material Available: Details of structure solution and refinement and tables of distances and angles and atomic coordinates and thermal parameters for **2b** and **2d** (17 pages); listings of observed and calculated structure factors for **2b** and **2d** (41 pages). Ordering information is given on any current masthead page.

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(30) Bis(cyclohexadienyl) complexes have been prepared from **2a**, **2b**, and **2c** and an η^4-triene containing a highly reactive exocyclic double bond has been synthesized from **2d**.

Synthesis and Structures of Dibenzometallacyclohexa-2,5-dienes

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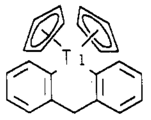
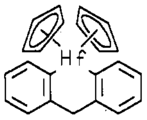
Summary: A study of the synthesis and structure of dibenzometallacyclohexa-2,5-dienes incorporating titanium, hafnium, and cobalt is reported. The crystal structures of the titanacycle and cobaltacycle exhibit boat conformations. Variable-temperature ^1H NMR data implicate fast-exchange spectra for boat–boat interconversion in the titanacycle and hafnacycle.

The importance of unsaturated transition metallacycles has been recently exemplified by their implication in stoichiometric and catalytic reactions.[1] Two stable metallacyclohexa-2,4-dienes have been reported. Hughes and co-workers recently reported the synthesis of a platinacyclohexadiene[2] and Bleeke and co-workers reported the isolation of an iridacyclohexadiene.[3] We here report a study of the preparation and characterization of the first metallacyclohexa-2,5-dienes—dibenzotitanacyclohexa-2,5-diene (**1**), dibenzohafnacyclohexa-2,5-diene (**2**), and dibenzocobaltacyclohexa-2,5-diene (**3**). The titana- and hafnacycles also constitute the first reported unsaturated six-membered metallacycles incorporating early transition metallacycles.[4]



1



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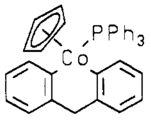
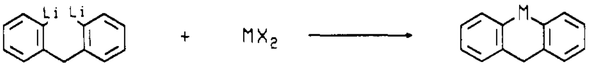


3

As a systematic approach toward the preparation of metallacyclohexadienes we sought a method which would favor forming both single bonds to the metal in one step. Much precedent is available in transition-metal chemistry in which dibenzometallacyclopenta-2,4-dienes may be prepared utilizing 2,2′-dilithiobiphenyl with transition-metal dihalides.[5] In that the kinetic stability of the diaryl transition-metal products is evident, we sought to react 2,2′-dilithiodiphenylmethane[6] with selected transition-metal dihalides to prepare the benzannulated six-membered metallacycles (eq 1). Initial attempts at this approach with titanocene dichloride gave mixtures of products with predominately unidentified yellow precipitates. However, slow addition of a solution (Et_2O) of the dilithium reagent to a cold (−78 °C) ether solution of titanocene dichloride, with *rigorous exclusion of light*, gave a red solution. After the solution was warmed to room temperature, washed with pentane and water, and dried with $MgSO_4$, removal of the solvent gave red needles



(1)

$MX_2 = (C_5H_5)_2TiCl_2$ — $\underline{1}$ $M = (C_5H_5)_2Ti$
$(C_5H_5)_2HfCl_2$ — $\underline{2}$ $M = (C_5H_5)_2Hf$
$(C_5H_5)(PPh_3)CoI_2$ — $\underline{3}$ $M = (C_5H_5)(PPh_3)Co$

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(1) (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (b) Hillard, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 4058. (c) Naiman, A.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 708. (d) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1979**, *101*, 215. (e) Katz, T. J.; Savage, E. B.; Lee, S. J.; Nair, M. *J. Am. Chem. Soc.* **1980**, *102*, 7944. (f) Katz, T. J.; Lee, S. J.; Nair, M.; Savage, E. B. *J. Am. Chem. Soc.* **1980**, *102*, 7942. (g) Tebbe, F. N.; Harlow, R. L. *Ibid.* **1980**, *102*, 6149. (h) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *Ibid.* **1981**, *103*, 5584. (i) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363–5364. (j) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737–738. (k) Wengrouvius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3923. (l) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574–1583 and references cited therein. (m) Tang, P.-C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132–1133. (n) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463–465. (o) Ferede, R.; Hinton, J. F.; Korfmacher, W. A.; Freeman, J. P.; Allison, N. T. *Organometallics* **1985**, *4*, 614–616. (p) Mike, C. A.; Ferede, R.; Allison, N. T. *Organometallics* **1988**, *7*, 1457.

(2) Hughes, R. P. *J. Chem. Soc., Chem. Commun.* **1986**, 1694.

(3) Bleeke, J. R.; Pneg, W.-J. *Organometallics* **1987**, *6*, 1576–1578.

(4) A saturated six-membered titanacycle has been reported: Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7418–7420.

(5) (a) Rausch, M. D.; Klemann, L. P. *J. Chem. Soc., Chem. Commun.* 1971, 354. (b) Rausch, M. D.; Gordon, H. B.; Samuel, E. J. *J. Coord. Chem.* **1971**, *1*, 141. (c) Wakatsuki, Y.; Nomura, O.; Hiroatsu, T.; Yamazaki, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1344. (d) Rausch, M. D.; Gordon, H. B.; Gardner, S. A. *J. Organomet. Chem.* **1973**, *60*, 179.

(6) Bickelhaupt, F.; Jongsma, C.; DeKoe, P.; Lourens, R.; Mast, N. R.; Van Mourik, G. L.; Vermeer, H.; Weustink, R. J. M. *Tetrahedron* **1976**, *32*, 1921.

0276-7333/88/2307-2573$01.50/0