Reductive Activation of the Coordinated Benzene in $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$: Synthesis and Characterization of the η^4-Naphthalene Complex $PPN[Mn(\eta^4\text{-}C_{10}H_8)(CO)_3]$

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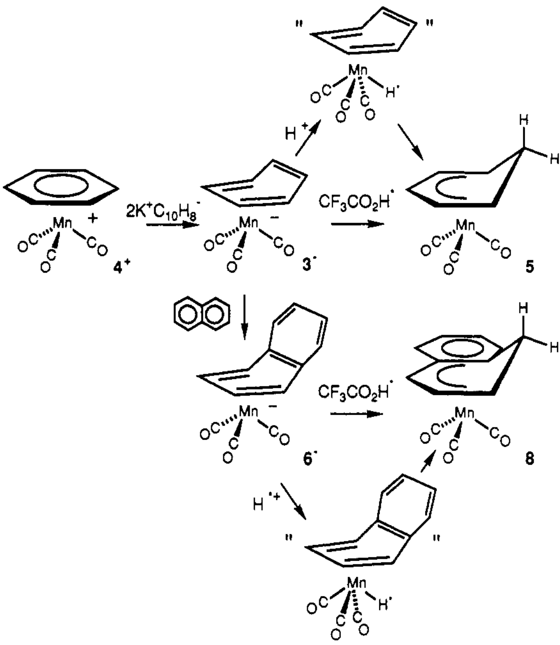
Summary: Naphthalenide reduction of $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]PF_6$ (**4PF$_6$**) in THF at −78 °C gives a solution of $[Mn(\eta^4\text{-}C_6H_6)(CO)_3]^-$ (**3$^-$**). The η^4-benzene in **3$^-$** can be protonated to give $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**5**). Attempted metathesis of **3$^-$** with PPNCl gave $PPN[Mn(\eta^4\text{-}C_{10}H_8)(CO)_3]$ (**PPN6**), established crystallographically to contain an η^4-naphthalene ligand. This is activated toward protonation to give $[Mn(\eta^5\text{-}C_{10}H_9)(CO)_3]$ (**8**). Labeling studies with CF_3CO_2D have established endo selective protonation of **3$^-$** and **6$^-$**, suggesting a metal-mediated pathway.

We recently reported that naphthalenide reduction of $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ (1) resulted in activation of the coordinated benzene toward electrophiles[1,2] and proposed that the reductive activation is associated with a hapticity shift of the benzene ligand from η^6 coordination in 1 to η^4 coordination in the intermediate dianionic carbonylmetalate $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$ (2^{2-}).[1,2] It has been proposed that η^6 to η^4 hapticity shifts may play a key role in substitution reactions of arene complexes[3] and may be of particular importance in the transition-metal-catalyzed hydrogenation of arenes,[4] but well established examples of η^4-arene complexes remain unusual.[5,6] Our synthetic approach to reduction of η^6-arene complexes is complementary to recent electrochemical studies by Finke[12] and by Geiger,[8] and the possibility that the isoelectronic but less highly charged manganese complex $[Mn(\eta^4\text{-}C_6H_6)(CO)_3]^-$ (3^-) might be more stable than 2^{2-} has led us to examine two-electron reduction of $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ (4^+).[13,14] We now wish to report (Scheme I) that 4^+ can indeed be reduced to a monoanionic carbonylmetalate, formulated as 3^-, in which the benzene is activated with respect to protonation to give $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (5). We have also observed, however, that 3^- is activated with respect to arene exchange with free naphthalene to give $[Mn(\eta^4\text{-}C_{10}H_8)(CO)_3]^-$ (6^-), and single-crystal X-ray diffraction studies have established that the naphthalene in PPN6 does indeed adopt the η^4-coordination mode.

Scheme I



In a typical reduction, dropwise addition of 5.2 mL of a 0.29 M solution of $KC_{10}H_8$ in tetrahydrofuran (THF)[15]

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(6) η^4 coordination has been established crystallographically for substituted benzene[7,8] and for naphthalene[9,10] ligands, and there is spectroscopic evidence for η^4-arene coordination in a number of other systems,[11] but there are no structurally characterized η^4 complexes of benzene itself.

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to a slurry of $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]PF_6$ ($4PF_6$, 0.24 g, 0.66 mmol) in THF (20 mL) at 78 °C resulted in formation of a reddish brown solution with $C\equiv O$ stretching absorptions at 1945 (vs), 1860 (s), and 1830 (s) cm^{-1}, consistent with formation of a monoanionic tricarbonyl complex such as 3^-.

As in the case of isoelectronic $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$ (2^{2-}),[1,2] the aromatic ligand in 3^- is activated toward protonic acids. Reaction of a freshly prepared solution of 3^- with 60 μL of neat CF_3CO_2H (0.78 mmol) at −78 °C results in replacement of the red-brown of the reduced solution with yellow-orange, while IR spectra showed that the stretching absorptions assigned to 3^- had been replaced by bands at 2020 (s) and 1950 (s, br) cm^{-1} assigned to the cyclohexadienyl complex $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**5**) (first prepared by hydride addition to 4^+[14]). The reaction was complete within seconds at −78 °C, and **5** (IR, ^1H NMR) could be isolated in 63% crude yield and 42% purified yield (0.09 g, 0.41 mmol) following chromatography on alumina with pentane.

Attempts to isolate 3^- by counterion exchange were frustrated by facile naphthalene exchange to give $[Mn(\eta^4\text{-}C_{10}H_8)(CO)_3]^-$ (6^-), which was the complex obtained (73% yield) as PPN**6**[16] ($PPN^+ = [Ph_3PNPPh_3]^+$) following attempted metathesis with PPNCl (1 equiv) in THF. Initial formulation of 6^- as an η^4-naphthalene complex was based primarily on its ^{13}C NMR characteristics,[16] which are very similar to those of $[Cr(\eta^4\text{-}C_{10}H_8)(CO)_3]^{2-}$ (7^{2-}), similarly formulated by Rieke as an η^4-naphthalene complex on the basis of ^{13}C NMR data.[17] The substitution of naphthalene for benzene in 3^- is analogous to the arene exchange that we have observed in the isoelectronic chromium system[3b]—although 3^- is less reactive than 2^{2-} toward electrophiles, arene exchange appears to be at least as rapid in the manganese system as in the chromium system.

The η^4-naphthalene in 6^-, like that in 7^{2-},[17] is activated toward acids. Reaction of a solution of 6^- in THF (prepared by reducing a slurry of 0.29 g (0.80 mmol) of $4PF_6$ in THF and stirring the mixture at room temperature for 1 h) with 0.10 mL of CF_3CO_2H resulted in lightening of the red color to a yellow-orange and replacement of the characteristic absorptions of 6^- at 1945 (vs), 1860 (s), and 1830 (s) cm^{-1} with new bands at 2018 (s) and 1933 (s, br) cm^{-1} assigned to the η^5-benzocyclohexadienyl complex $[Mn(\eta^5\text{-}C_{10}H_9)(CO)_3]$ (**8**).[18] This material was isolated in 39% yield (0.085 g, 0.32 mmol) by a procedure in which the solvent was removed under reduced pressure, the product was extracted into Et_2O, the solvent was again removed, and the product was chromatographed with pentane on silica gel.

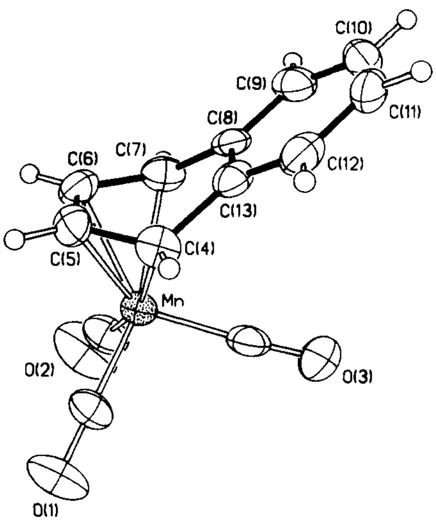

Figure 1. Structure of the anion in $PPN[Mn(\eta^4\text{-}C_{10}H_8)(CO)_3]$ (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): C(4)–C(5) = 1.440 (8), C(5)–C(6) = 1.378 (7), C(6)–C(7) = 1.438 (8), C(7)–C(8) = 1.455 (7), C(4)–C(13) = 1.483 (8), C(8)–C(13) = 1.411 (7); C(1)–Mn–C(2) = 88.0 (3), C(1)–Mn–C(3) = 99.8 (2), C(2)–Mn–C(3) = 99.3 (3), diene centroid (cnt)–Mn–C(1) = 122.1 (2), cnt–Mn–C(2) = 124.6 (2), cnt–Mn–C(3) = 116.5 (2).

We have confirmed that the protonations of 3^- and 6^- are mechanistically similar, and closely related to protonations of isoelectronic 2^{2-} and 7^{2-},[1,17] by establishing that both protonations are predominantly endo, implying a metal-mediated pathway (Scheme I). This was demonstrated by labeling studies in which 3^- and 6^- were treated with CF_3CO_2D (0.15 M in Et_2O). Products were isolated by solvent removal under reduced pressure and extraction into diethyl ether (3 × 15 mL). The solvent was removed again, and the **5** and **8** obtained were purified by chromatography on silica gel in pentane. ^1H NMR spectroscopy established in each case that there was no deuteration in the exo position and 64 ± 5% and 89 ± 5% deuteration respectively in the endo position.[19]

Although the isolation of PPN**6** prevented characterization of 3^-, it has allowed us for the first time to characterize structurally an η^4-arene carbonylmetalate complex, and an X-ray diffraction study[20] has established unambiguously that the arene ligand in 6^- does indeed adopt an η^4 conformation as shown in Figure 1. The dihedral angle of 37.1° between the coordinated diene and the exo benzene in 6^- is consistent with η^4 coordination and is similar to the value of 43.0° observed by Wreford and Foxman for $[Ta(\eta^4\text{-}C_{10}H_8)(Me_2PCH_2CH_2PMe_2)_2Cl]$[9]—this and $[Ru(\eta^4\text{-}C_{10}Me_8)(\eta^6\text{-}C_6Me_6)]$[10] are the only other structurally characterized complexes containing η^4-naphthalene ligands. Determination of an η^4-coordination

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(16) IR (THF, $\nu_{C\equiv O}$ only): 1940 (s), 1852 (s), 1835 (s) cm^{-1}. ^1H NMR (CD_3CN): δ 6.12 (s, 4 H, H_{5-8}), 5.70 (m, 2 H, $H_{2,3}$), 2.44 (m, 2 H, $H_{1,4}$). ^{13}C NMR (CD_3CN): δ 241.0 (s, CO), 149.0 (s, $C_{9,10}$), 121.5 (d, $^1J_{CH}$ = 155 Hz, $C_{5,8}$ or $C_{6,7}$), 119.0 (d, $C_{6,7}$ or $C_{5,8}$), 83.9 (d of t, $^1J_{CH}$ = 167 Hz, $^3J_{CH}$ = 6 Hz, $C_{2,3}$), 57.6 (d, $^1J_{CH}$ = 151 Hz, $C_{1,4}$). Anal. Calcd for $C_{49}H_{38}MnNO_3P_2$: C, 73.04; H, 4.76. Found (Galbraith, Knoxville, TN): C, 71.93; H, 4.93.

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(18) IR ($\nu_{C\equiv O}$ only, THF): 2018 (s), 1933 (s, br) cm^{-1}. IR (pentane): 2024 (s), 1948 (vs), 1934 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 6.74 (d, 1 H, J = 8.3 Hz, H_5), 6.68 (m, 1 H, J = 7.5, 1.4 Hz, H_6), 6.56 (m, 1 H, J = 7.5, 1.4 Hz, H_7), 6.51 (d, 1 H, J = 8.1 Hz, H_8), 5.76 (d, 1 H, J = 5.3 Hz, H_4), 4.59 (t of d, 1 H, J = 6.4, 0.9 Hz, H_3), 2.80 (d of d, 1 H, J = 14, 5.2 Hz, H_{endo}), 2.74 (t of t, 1 H, J = 6.2, 1.0 Hz, H_2), 2.20 (d, 1 H, J = 14 Hz, H_{exo}). ^{13}C NMR (CD_2Cl_2): δ 224.6 (s, CO), 133.7 (d of d, $^1J_{CH}$ = 159 Hz, $^3J_{CH}$ = 8 Hz, C_5), 129.9 (d of d, $^1J_{CH}$ = 159 Hz, $^3J_{CH}$ = 8 Hz, C_6), 129.6 (d of d, $^1J_{CH}$ = 161 Hz, $^3J_{CH}$ = 8 Hz, C_7), 128.6 (d of d, $^1J_{CH}$ = 162 Hz, $^3J_{CH}$ = 8 Hz, C_8), 110.0 (s, C_{10}), 97.0 (d, $^1J_{CH}$ = 164 Hz, C_4), 93.4 (s, C_9), 74.4 (d, $^1J_{CH}$ = 173 Hz, C_3), 48.9 (d, $^1J_{CH}$ = 161 Hz, C_2), 30.5 (t, $^1J_{CH}$ = 133 Hz, C_1). Anal. Calcd for $C_{13}H_9MnO_3$: C, 58.23; H, 3.38. Found (Atlantic Microlab, Norcross, GA): C, 58.01; H, 3.43.

(19) The failure to incorporate a full 1 equiv of deuterium into **5** or **8** (confirmed by mass spectral analysis) implies an exchange process during or after protonation. The nature of this exchange is undetermined, but it is related to sample history. In the naphthalene case we have seen exchange percentages ranging from 70% to 89%, but in no case have we seen deuterium incorporated into the exo position. We believe that the exchange is probably base catalyzed.

(20) Crystal data: monoclinic space group Ia, $Z = 4$, a = 14.677 (2) Å, b = 20.549 (3) Å, c = 13.817 (2) Å, β = 91.17 (1)°, d_{calc} = 1.284 g cm^{-3}, μ = 4.6, λ(MoKα) = 0.710 73 Å. Of the 6748 reflections measured in the range $4 < 2\theta < 48°$, 5102 unique data with $F_o \geq 3\sigma(F_o)$ were used in the structure solution by direct methods. The phenyl rings of the cation were constrained to rigid, planar hexagons, and hydrogen atoms were treated as idealized contributions. Refinement converged at R = 4.76% and R_w = 5.08%, with GOF = 0.99. Full details of the structure determination will be published elsewhere.

mode for the reductively activated naphthalene in 6^- does not unambiguously establish η^4 coordination for the reductively activated benzene ligands in 3^- and 2^{2-}, but, given the similarities in the course of protonation of 6^-, 3^-, 2^{2-}, and 7^{2-}, the proof of η^4 coordination for the naphthalene ligand in 6^- strongly supports our hypothesis of η^4-coordination in 2^{2-} and 3^-.

Acknowledgment. We thank the National Science Foundation for financial support through Grant No. CHE-8722424.

Note Added in Proof. Wey and Butenschön have recently reported that the ^{13}C NMR spectrum of 3^- confirms η^4 coordination of the benzene ligand.[21]

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Nonorganometallic Pathway of the Passerini Reaction Assisted by $TiCl_4$

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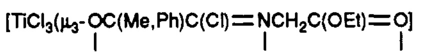
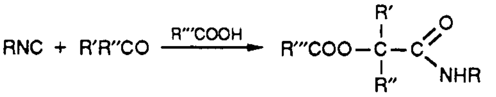
Summary: The reaction of $TiCl_4$ with different isocyanides did not lead to any insertion of the isocyanide functionality into the Ti–Cl bond but to simple adducts such as $\{[TiCl_3(2,6\text{-}Me_2C_6H_3NC)]_2(\mu_2\text{-}Cl)_2\}$, $[(TiCl_4)_2(\mu_2\text{-}O{=}P(OEt_2CH_2NC)_2]$, and $[(TiCl_4)_2(\mu_2\text{-}O{=}C(OEt)CH_2NC)_2]$. This ruled out any organometallic pathway in the Passerini reaction assisted by $TiCl_4$. The present mechanism is proposed on the basis of the isolation and structural characterization of the key intermediate



$$[TiCl_3(\mu_3\text{-}OC(Me,Ph)C(Cl){=}NCH_2C(OEt){=}O)]$$

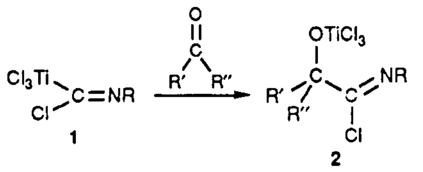
derived from the reaction of $PhCOCH_3$ and $CNCH_2COOEt$ assisted by $TiCl_4$.

Several mechanisms[1] have been proposed for the reaction of a carbonyl compound with an isocyanide assisted by a carboxylic acid, known as the Passerini[2] reaction, which produces the ester of an α-acyloxy amide (eq 1).



$$\mathrm{RNC} + \mathrm{R'R''CO} \xrightarrow{\mathrm{R'''COOH}} \mathrm{R'''COO}-\overset{\mathrm{R'}}{\underset{\mathrm{R''}}{\mathrm{C}}}-\mathrm{C}(=\mathrm{O})\mathrm{NHR} \qquad (1)$$

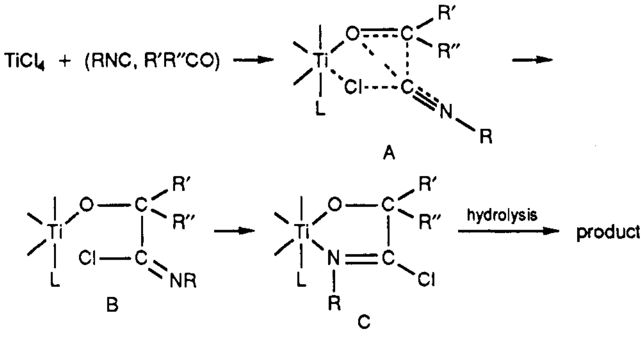
In a variation of the Passerini reaction the acid employed was $TiCl_4$.[3] For such a version the organometallic pathway (2) has been proposed.[3]



(2)

The mechanism proposed in reaction 2 is essentially based on the intermediacy of an organometallic derivative from a nonorganometallic precursor[3,4] (complex 1) and the formation of an intermediate (complex 2) by the insertion of a carbonyl function into a Ti–C σ bond.[3] Studying the reaction of $TiCl_4$ and isocyanides, we found, in contrast to reports in the literature,[4] that, independent of the stoichiometry, the solvent, and the nature of the substituent at the isocyanide ligand, simple adducts are formed rather than insertion products such as 1.[5] This is exemplified by the isolation and structural characterization of $[TiCl_4(CNBu^t)_2]$[5] (3), $\{[TiCl_3(2,6\text{-}Me_2C_6H_3NC)]_2(\mu_2\text{-}Cl)_2\}$[6] (4), $[(TiCl_4)_2(\mu_2\text{-}O{=}P(OEt)_2CH_2NC)_2]$[6] (5), and $[(TiCl_4)_2(\mu_2\text{-}O{=}C(OEt)CH_2NC)_2]$[6] (6). The insertion of the isonitrile into the Ti–Cl bond was mainly supported by an IR spectrum showing, when taken in air, a strong band at around 1625 cm^{-1}.[5] This band belongs, however, to the formamide derived from the hydrolysis of RNC. In accord with the adduct formation, metal-bonded isocyanides in 3–6 have a C–N stretching higher than that

Scheme I



L = RNC, R′R″CO, μ-Cl, donor atom on R

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(6) Details are reported for the preparation of **6** only: The slow addition of $TiCl_4$ (2.0 mL, 3.47 g, 18.3 mmol) to a CH_2Cl_2 (100 mL) solution of $CNCH_2COOEt$ (2.0 mL, 2.07 g, 18.3 mmol) gave a yellow solid (93%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.64 (s, 2 H, CH_2), 4.33 (q, 2 H, Et), 1.33 (t, 3 H, Et). ν(CN) (Nujol): 2254 cm^{-1} (2165 cm^{-1} in the free isocyanide). Complex **4**: ν(CN) (CH_2Cl_2 solution) 2200 cm^{-1} (vs 2123 cm^{-1} in the free ligand). Complex **5**: ν(CN) (Nujol) 2245 cm^{-1} (vs 2153 cm^{-1} in the free ligand). The structures of **3**,[5] **4**, and **5** have been determined by an X-ray analysis (Carofiglio, T.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C., unpublished results).

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