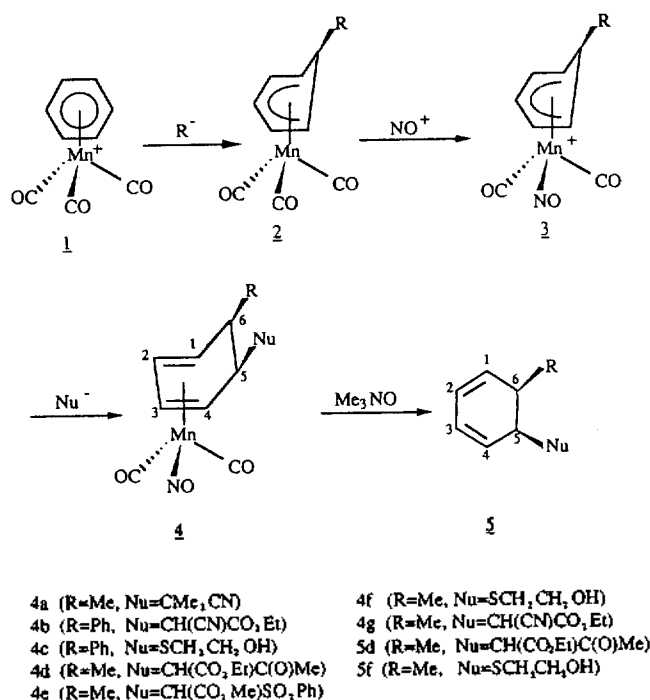


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Scheme 1.

It recently has been demonstrated² that the manganese-mediated functionalization of arene is a promising synthetic procedure. Thus, the addition of phosphorus, hydride and carbon donor nucleophiles to (arene) Mn(CO)₃⁺, **1**, occurs with high regio- and stereo-selectivity.³ Replacement of a CO ligand in **2** by NO⁺ produces cationic complexes, **3**, that rapidly react with phosphorus, nitrogen, and hydride donors at the carbon adjacent to the saturated carbon.^{2,4} However, when the second nucleophile was a carbanion, the double nucleophilic addition was not possible because electron transfer might occur.² In general, addition of Grignard reagent or RLi to complex **3** results in a mixture of products of type **2** and **4**, often in poor yield.² NaCH(CO₂Me)₂ was found to add to **3** to give the cyclohexadiene complex **4**.² Since complexes **3** offer a unique means of synthesizing cyclohexadiene derivatives, we decided to investigate the reactions between complex **3** and some nucleophiles.

We commence by describing some preliminary, less successful experiments performed on complex **3** with LiCMe₂CN, which will be seen to contrast with the soft nucleophile addition. Treatment of **3** with LiCMe₂CN (THF, -78 °C) resulted in a low yield (2.9%) of product **4a**, together with ca 12% yield of **2** (R=CMe₂CN)⁵, the latter being indicative of electron-transfer processes. The relative yield of **2** (R=CMe₂CN) increased as the reaction time increased, and finally **2** (R=CMe₂CN) was obtained as a sole product. Most likely this is due to the instability of the ring product **4** in the presence of large excess of carbanion.

Reaction of **3** (R=Me or Ph) with stabilized enolates such as NaCH(CO₂Me)₂,² NaCH(CO₂Et)C(O)Me,⁵ NaCH(CO₂Et)CN,⁵ NaCH(CO₂Me)SO₂Ph,⁵ and sulfur-donors such as NaSCH₂CH₂OH⁵ and the desired ring adduct **4** was formed in a reasonable yield. We summarized the results in Scheme 1. The above results indicate the nucleophilic addition **3** is

Double Nucleophilic Addition to (Arene)manganesetricarbonyl Cation *via* (Cyclohexadienyl)manganesedicarbonylnitrosyl Cations

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Double nucleophilic addition to coordinated arenes has been reported with several other complexes,¹ but usually the reported procedure cannot be readily generalized to include a variety of nucleophiles.

dependent on the nature of nucleophile. The large vicinal coupling constant $J(H-5, H-6)$ of ca 10.8 Hz shows that the nucleophiles are situated *exo*.

The mechanism of reactions between **3** and nucleophiles such as P-donors is a simple bimolecular attack.⁶ For $P(p-C_6H_4X)_3$ addition to $\mathfrak{M}(R=Me)$ a Hammett plot ($\log k$ vs. σ) has a slope = -1.0 and a Bronsted plot ($\log k$ vs. $pK_a(H_2O)$) has a slope $\alpha=0.47$. These values are analogous to ones obtained previously for tertiary phosphine additions to other coordinated π -hydrocarbon systems.⁷ They are also very similar to values obtained for tertiary phosphine attack on EtI and $PhCH_2Cl$ ⁸, for which an early transition state has been established. The Bronsted slope of 0.47 shows that nucleophilic basicity is quite important, in contrast to nucleophilic attack at soft metal centers like Pt^{II} , for which is close to zero.⁹ The kinetic study for the addition of phosphorus donors to **3** suggested that the complex **3** could be classified as a hard electrophile. This contradicts the addition of stabilized enolates addition to **3**. However, we would prefer complex **3** to be soft. When one of the carbonyl groups of **3** was substituted by phosphite, we expected that the softness of the salt would increase. As we expected, reaction of the phosphite-substituted manganese nitrosyl cation with stabilized carbanions gave very high yields of ring-adducts.⁵ Similar experimental observations were reported for cycloheptadienyliron complexes.¹⁰ Sweigart¹¹ reported the addition of the carbanion of malonate to the phosphine-substituted manganese nitrosyl cation. This suggested that the softness of **3** was very important to the addition of stabilized carbanions. It is difficult at this stage to completely rationalize the observation, but it would seem that further information is desirable.

When the nucleophiles were $NaCH(CO_2Et)C(O)Me$, $NaCH(CO_2Et)SO_2Ph$ and $NaCH(CO_2Et)CN$, we consistently observed the formation of two isomeric compounds in TLC, which could not be separated by column chromatography. We could confirm the two isomeric mixture by means of ¹³C-NMR spectrum of the compound **4** and ¹H-NMR spectrum of the demetallated compound **5**.

Application of the above methodology to organic synthesis requires that we be able to remove the metal from complexes **4** cleanly and high yield and further manipulate the liberated dienes. The substituents such as malonate would be ideally suited for further reaction, e.g., cyclofunctionalization. The complexes **4** were readily demetallated by using the amine oxide method, viz, the complex was treated with excess anhydrous trimethylamine N-oxide in benzene at 80°C for 5–10 h, giving the substituted cyclohexadiene derivative **5** in a reasonable yield.⁵

In conclusion, we have now demonstrated that (a) the soft nucleophiles add to complex **3** to give the ring-adduct **4** and (b) the metal can be successfully removed in high yield in the presence of functional groups. We have shown that the manganese mediated conversion of coordinated arenes to coordinated cyclohexadienes can be a facile procedure that may prove quite useful in synthesis.

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5. **4a**(R=Me), yield 2.9%; IR ν_{CO} 2023, 1970 cm^{-1} , ν_{NO} 1730 cm^{-1} ; EI-MS, m/z , 246(M^+-2CO), 216($M^+-2CO-NO$), 161($m^+-Mn(CO)_2NO$). **4b**(R=Ph), IR ν_{CO} 2040, 1980 cm^{-1} , ν_{NO} 1740 cm^{-1} ; ¹H NMR($CDCl_3$) δ 7.2–7.4(m, 5H, Ph), 5.8(m, 2H, $H^{2,3}$), 4.14(q, 7.0 Hz, 2H, CH_2), 4.0(m, 1H, H^4), 3.69(dd, 10.8, 3.0 Hz, 1H, H^5), 3.25(m, 1H, H^5), 3.15(dd, 8.0, 3.0 Hz, 1H, H^1), 2.91(d, 6.3 Hz, 1H, CH), 1.25(t, 7.0 Hz, 3H, CH_3) ppm; EI-MS, m/z , 352(M^+-2CO), 322($M^+-2CO-NO$), 267($M^+-Mn(CO)_2NO$), 210($M^+-CH(CO_2Et)CN$). **4c**(R=Ph), IR ν_{CO} 2025, 1970 cm^{-1} , ν_{NO} 1730 cm^{-1} ; ¹³C NMR(d_6 -benzene) δ 142.8, 130.0, 127.8, 127.0(Ph), 88.6, 88.0, 70.9, 70.1(OCH_2), 48.8, 47.5, 35.6, 30.1(SCH_2) ppm; EI-MS, m/z , 345(M^+-CO), 317(M^+2CO), 287($M^+-2CO-NO$), 232($M^+-Mn(CO)_2NO$). **4d**(R=Me), yield 66.6%; IR ν_{CO} 2030, 1975, 1720 cm^{-1} , ν_{NO} 1732 cm^{-1} ; ¹³C NMR(d_6 -benzene) δ major isomer; 200.0(C(O)), 168.2(CO_2), 89.4, 86.3, 73.5, 65.8, 32.8, 28.2(ring carbons), 61.0(CH_2CH_3), 39.2(CH), 29.9($CH_3C(O)$), 21.9(Me), 13.7(CH_2CH_3), minor isomer; 200.0(C(O)), 168.4(CO_2), 89.4, 86.3, 73.5, 66.8, 33.5, 29.0(ring carbons), 61.0(CH_2CH_3), 39.8(CH), 29.9($CH_3C(O)$), 21.9(Me), 13.7(CH_2CH_3) ppm; EI-MS, m/z , 307(M^+-2CO), 277($M^+-2CO-NO$), 262($M^+-2CO-NO-Me$), 234($M^+-2CO-NO-Me-C(O)Me$). **4e**(R=Me), yield 67.3%; IR ν_{CO} 2038, 1974 cm^{-1} , ν_{NO} 1737 cm^{-1} , ν_{SO_2} 1322, 1142 cm^{-1} ; ¹³C NMR($CDCl_3$) δ 222.3(CO), 137.7, 134.3, 129.4, 129.1 (Ph ring carbons), 52.5(OMe), major isomer, 166.5(CO_2) 89.5, 86.8, 72.4, 65.9, 33.8, 26.9(ring carbons), 39.4(CH), 22.0(Me), minor isomer 165.9(CO_2), 89.4, 86.7, 73.3, 65.4, 33.6, 26.9(ring carbons), 39.5(CH) 23.2(Me) ppm; EI-MS, m/z , 391(M^+-2CO), 360($M^+-2CO-NO-H$), 346($M^+-2CO-NO-Me$). **4f**(R=Me), yield 60.5%; IR ν_{CO} 2038, 1973 cm^{-1} , ν_{NO} 1737 cm^{-1} ; ¹³C NMR(d_6 -acetone) δ 221.7(CO), 86.4, 86.3, 71.6, 60.0, 46.8, 34.3(ring carbons), 68.0(OCH_2), 33.7(SCH_2), 22.7(Me) ppm; EI-MS, m/z , 225(M^+-2CO), 225($M^+-2CO-NO$), 210($M^+-2CO-NO-Me$). **4g**(R=Me), yield 59.1%; IR ν_{CO} 2030, 1970 cm^{-1} , ν_{NO} 1735 cm^{-1} ; ¹³C NMR (d_6 -benzene) δ major isomer. 165.9(CO_2), 116.8(CN), 89.7, 87.6, 73.4, 62.6, 40.8, 34.1(ring car-

bons), 40.8(CH) minor isomer, 165.4(CO₂), 89.4, 87.3, 73.0, 62.4, 41.4, 33.3(ring carbons), 41.4(CH), 64.5(OCH₂), 13.8(OCH₂CH₃), 21.2(Me) ppm. EI-MS, *m/z*, 290(M⁺-2CO), 260(M⁺-2CO-NO), 245(M⁺-2CO-NO-Me), 234(M⁺-2CO-NO-Me-CN). 5d. major isomer, ¹H NMR(CDCl₃) δ 5.9(m, 4H), 4.20(q, 7.2 Hz, OCH₂), 3.69(d, 2.9 Hz, CH), 3.31(m, 2H), 2.35(m, 2H), 2.26(s, C(O)CH₃), 1.27(t, 7.2 Hz, CH₃), 0.85(d, 7.1 Hz, CH₃) ppm; minor, ¹H NMR(CDCl₃) δ 5.9(m, 4H), 4.19(q, 7.1 Hz, OCH₂), 3.75(d, 2.2 Hz, CH), 3.3(m, 2H), 2.35(m, 2H), 2.27(s, C(O)CH₃), 1.28(t, 7.1 Hz, CH₃), 1.28(t, 7.1 Hz, CH₃), 0.81(d, 7.1 Hz, CH₃) ppm; 5f(R=Me, Nu=SCH₂CH₂OH), ¹H NMR(CDCl₃) δ 5.60~6.03(m, 4H), 2.90(m, 1H), 2.73(m, 1H), 3.71(br, OH), 3.41(t, 3.5 Hz, OCH₂), 2.66(t, 2.2 Hz, SCH₂), 1.27(d, 9.1 Hz, Me). [{MeC₆H₄(CH(CN)CO₂Et)}Mn(CO)NO(P(OPh)₃)] yield 81.6%, IR ν_{CO} 1967 cm⁻¹, ν_{NO} 1735 cm⁻¹, ν_{CO₂} 1720 cm⁻¹, ¹³C NMR(CDCl₃) δ 229.3(CO), 150.1, 128.8, 124.1, 120.1(P(OPh)₃), 116.4(CN), major isomer, 165.1(CO₂), 88.2, 84.4, 71.9, 60.2, 40.2, 32.9 (ring carbons), minor isomer, 164.6(CO₂), 88.0, 84.0, 71.7, 60.4, 40.6, 32.9(ring carbons), 61.7(OCH₂), 42.5, 42.1(CH), 20.5(Me), 12.9(OCH₂CH₃).

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A Voltammetric Procedure for Determinations of Four Main Constituents in Ancient Coins

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Quite often analytical chemists are asked for to analyze several analytes in the same sample or in a set (large numbers) of samples, in many cases, for the exploratory purposes.^{1,2} In this laboratory a rapid simple method is required which can be applied to the multicomponent analysis of coin samples for the purposes of pattern recognition. Samples for

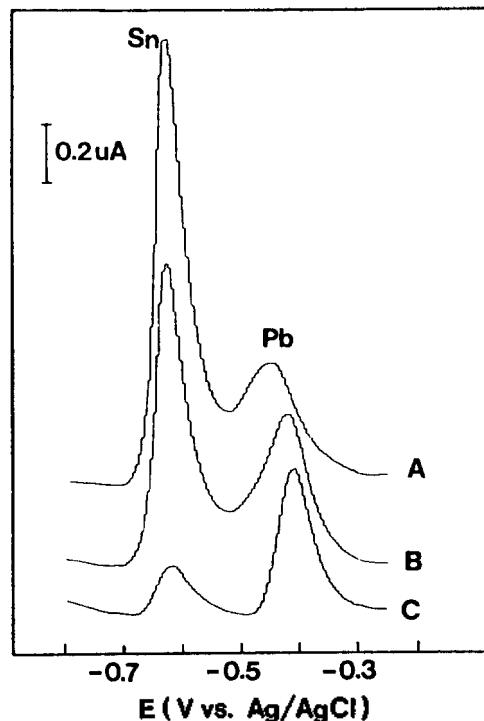


Figure 1. Typical DPAS voltammograms in 0.05 M, pH 8.0 sodium borate solution containing [Sn(IV)]= 2.5×10^{-6} M and [Pb(II)]= 2.7×10^{-7} M, showing the dependence of peak resolution on deposition potentials: A, -1.6V; B, -1.4V; C, -1.2V vs Ag/AgCl. Deposition time, 4 min. Scan rate, 10 mV/sec. Modulation amplitude, 5 mV. Pulse repetition time, 1 sec.

analysis were ancient coins (1423-1883 A.D.) having chemical compositions,³ 60-92% copper, 3-26% lead, 0.2-29% zinc, and 0.2-6% tin as the main constituents.

Recently there is a growing appreciation of the power of the pulse voltammetry for it provides multielement capability. It can offer the advantage of simultaneous multi-element determinations (four to six metals) at the lowest costs compared to other competing multianalyte techniques if a suitable experimental procedure is provided.⁴

The one-element-at-a-time nature of the most existing methods^{5,6} and the costs of ICP, X-ray fluorescence analysis⁷ and the limited availability of neutron activation analysis and their lacks of sensitivity (accordingly restriction to) certain metals suggest that the search for an electrochemical multimetal analysis scheme for the alloy samples is timely.

Ideally, a procedure employing only a single technique throughout the entire run is desirable, saying, that can detect the four main elements simultaneously and present their signals to the strip-chart recorder at a time with satisfactory resolutions. However it was not achievable because of the presence of stannic tin, which has peculiar behaviors and shows a great overlapping interference with lead.⁸ In this work, as the second best, the advantages of differential pulse polarography (DPP) for copper, lead, and zinc and anodic stripping voltammetry (ASV) for tin are combined.

In most cases (for both DPP and ASV), good chemistry is the proper solution to the resolution problem. One approach is to make choice of a supporting electrolyte medium. Preli-