THE USE OF N-BENZENETHIOPHTHALIMIDE AS A REAGENT IN ORGANOMETALLIC SYNTHESES: BENZENETHIOLATO- AND N-PHTHALIMIDOMETAL CARBONYL COMPLEXES

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Summary

The reaction between $PPN[CpW(CO)_3]$ ($PPN^+ = Ph_3PNPPh_3^+$) and N-benzenethiophthalimide (PhSphth) gives $CpW(CO)_3SPh$ and PPN[phth], and the organometallic compound was isolated in high yield. Contrasting results occur using $PPN[Mn(CO)_5]$ and $PPN[CpMo(CO)_3]$. Although the expected benzenethiolatometal complexes are detected as initial products, these species react further with the phthalimide anion ($phth^-$) to give phthalimidometal complexes. From a reaction using $PPN[Mn(CO)_5]$ and PhSphth in a 1/2 ratio one can isolate $PPN[Mn(CO)_4(phth)_2]$ in good yield. There is some evidence that PPN $[Mn(CO)_4(SPh)(phth)]$ is also an intermediate in this reaction. In a 1/1 ratio, these reagents give a mixture of $PPN[Mn(CO)_4(phth)_2]$ and $PPN[Mn_2(\mu-SPh)_3(CO)_6]$. Formation of $PPN[Mn(CO)_4(phth)_2]$ can also be accomplished by more traditional reactions between PPN[phth] and either $MnBr(CO)_5$ or $Mn_2(\mu-Br)_2(CO)_8$. A single crystal X-ray diffraction study provides the structure of $PPN[Mn(CO)_4(phth)_2]$. The reaction between $PPN[CpMo(CO)_3]$ and PhSphth gives $CpMo(CO)_3SPh$ which is rapidly converted to a species believed to be $PPN[CpMo(CO)_2(phth)_2]$. Isolation of this unstable compound was not accomplished.

Introduction

Reagents which function as donors of electrophilic RS^+ groups include $[Me_2SSMe]BF_4$, PhSCl, and PhSphth (phth = the phthalimido group), this reactivity presumably being the result of $RS^{\delta+}-X^{\delta-}$ polarity of the sulfur–non metal bond. The first listed species has found recent substantial use in organic syntheses [1]. We have reported its use in the syntheses of organometallic complexes with thiolate ligands [2]. Various RSphth reagents have found synthetic utility in organometallic chemistry [3,4] and in coordination chemistry [5]; in these examples, an RS^+ group is usually found to add to a coordinated ligand group to give the observed product.

Oxidative addition of the N–S bond in RSSphth to a platinum(0) species is also mentioned [3].

In conjunction with studies on the synthesis of organometallic thiolate complexes using RS$^+$ donors, we carried out reactions between *N*-benzenethiophthalimide (PhSphth) and several metal carbonyl anions. The expected benzenethiolatometal carbonyl complex is apparently the initial product in each reaction. However, in only one instance (the reaction with PPN[CpW(CO)$_3$]) was this the isolated product. In reactions of PPN[CpMo(CO)$_3$] and PPN[Mn(CO)$_5$] with PhSphth the initially formed product reacted further with the phthalimide ion produce a phthalimidometal complex. The isolable manganese complex, PPN[Mn(CO)$_4$-(phth)$_2$], was also synthesized from PPN[phth] and MnBr(CO)$_5$ or Mn$_2(\mu$-Br)$_2$(CO)$_8$, and its structure determined by X-ray crystallography.

Experimental

Synthesis of PhSphth [6], PPN[Mn(CO)$_5$], PPN[CpMo(CO)$_3$] and PPN[Cp-W(CO)$_3$] [7], MnBr(CO)$_5$ [8], Mn$_2(\mu$-Br)$_2$(CO)$_8$ [9] and [Mn(CO)$_5$(MeCN)]PF$_6$ [10] were carried out by standard procedures. Samples of PPN[phth] were prepared by deprotonation of phthH with one equivalent of NaOMe in methanol, followed by metathesis with [PPN]Cl in CH$_2$Cl$_2$. Solvents were dried by standard methods and all manipulations were carried out under dry N$_2$. Infrared spectra were recorded on a Beckman Model 4230 spectrophotometer, and ^{1}H NMR spectra were obtained with an IBM WP-270 spectrometer. Mass spectrometric data were obtained on an AEI-MS-902 mass spectrometer. Analysis were performed by the Galbraith Laboratory, Knoxville, TN.

Typically, the progress of reactions described below was monitored by recording infrared spectra (ν(CO)) of aliquots of the reaction mixture taken at various times. This procedure was useful in detecting intermediates and in defining conditions necessary for complete reaction.

Reaction of PPN[CpW(CO)$_3$] and PhSphth. A solution of PhSphth (0.15 g, 0.59 mmol) in 10 ml CH$_2$Cl$_2$ was added to a solution of PPN[CpW(CO)$_3$] (0.20 g, 0.23 mmol) in 40 ml of CH$_2$Cl$_2$ at ambient temperature. An infrared spectrum taken immediately after mixing indicated that complete conversion to CpW(CO)$_3$SPh had occurred. When, after 2 h, no subsequent reaction occurred the solvent was removed under reduced pressure. The residue that remained was dissolved in Et$_2$O and placed on an alumina chromatographic column. Elution using Et$_2$O gave a single red band which was collected. Evaporation of solvent followed by recrystallization of the residue gave 0.080 g of CpW(CO)$_3$SPh (80% yield). This known compound [11] was identified based on infrared (ν(CO) at 2034s, 1947s cm^1 in CH$_2$Cl$_2$) and ^{1}H NMR data (δ 5.70s, C$_5H_5$ in CDCl$_3$).

Reactions of PPN[Mn(CO)$_5$] and PhSphth. Samples of PhSphth (0.60 g, 2.4 mmol) and PPN[Mn(CO)$_5$] (1.0 g, 1.3 mmol) were placed in a flask and 200 ml CH$_2$Cl$_2$ added. The mixture was stirred at ambient temperature for 20 min. An infrared spectrum taken at this point contained peaks at 2075w, 1997vs, 1972s, 1923s, 1915vs, and 1640 cm^{-1}. The solution was concentrated under vacuum and hexane added, causing precipitation of a tan solid which was removed by filtration. Evaporation of the remaining solution yielded a bright yellow solid. This was dissolved in acetone and chromatographed on a short (4 cm) neutral alumina

column, a single yellow band eluting with acetone. Collection of this band followed by evaporation of solvent in vacuo produced a yellow solid. This was crystallized from CH_2Cl_2/hexane to give a pure sample of the product, $PPN[Mn(CO)_4(phth)_2]$ (0.6 g., 50%; m.p. darkens ~ 150°C, decomp > 185°C).

Anal.: Found: C, 67.57; H, 4.10; N, 4.51. $C_{56}H_{38}MnN_3O_6P_3$ calcd.: C, 67.41; H, 3.84; N, 4.21%. IR (CH_2Cl_2): 2090w, 2004s, 1980ms, 1928s, 1649vs, 1625s, 1607s cm^{-1}.

We have carried out this same reaction at −26°C. An aliquot was taken from the reaction mixture after about 1 min and its infrared spectrum recorded. Carbonyl absorptions were seen at 2126w, 2038m, 2008m cm^{-1}, along with absorptions at 2090vs, 2023s, 1980m and 1930s cm^{-1}. The first three absorptions confirm [2] the presence of $Mn(SPh)(CO)_5$. The reaction mixture was allowed to stand at −26°C for about 4 h, during which time the absorptions due to this species slowly decreased in intensity while absorptions due to $PPN[Mn(CO)_4(phth)_2]$ increased. Workup of this reaction (after warming) led to isolation of this product.

With a 1/1 ratio of reactants for this reaction, a slightly different result is obtained. The initial solution, 20 min after mixing of the reactants, gives the same infrared spectrum as seen for the 1/2 reaction, i.e., $\nu(CO)$ at 2075w, 1997vs, 1972s, 1923s, 1915vs, and 1640s cm^{-1}. A workup of the reaction mixture at this point produced a mixture of $PPN[Mn(CO)_4(phth)_2]$ and $PPN[Mn_2(\mu\text{-}SPh)_3(CO)_6]$ ($\nu(CO)$ at 1997s, 1918s, 1908sh cm^{-1}, for the tetraethylammonium salt [12]). The mixture can be separated by fractional crystallization using CH_2Cl_2/hexane mixture in which $PPN[Mn(CO)_4(phth)_2]$ is more soluble. The two species were identified by comparison of infrared and m.p. data with values for known samples.

Reactions of MnBr(CO)$_5$ and PPN[phth]. Samples of $MnBr(CO)_5$ (0.20 g, 0.73 mmol) and PPN[phth] (0.50 g, 0.73 mmol) were dissolved in 100 ml CH_2Cl_2. After stirring the solution for 2 h, the solvent was removed in vacuo leaving a sticky residue. This was extracted with 100 ml Et_2O. Filtration, followed by evaporation of the filtrate, produced an orange solid. This product, $Mn(CO)_5(phth)$ (0.024 g, 10% yield) was recrystallized from CH_2Cl_2/hexane.

Anal. by MS peak match: found: 340.9353. $^{12}C_{13}{}^1H_4{}^{55}Mn^{14}N^{16}O_5$ calc.: 340.9367. IR (CH_2Cl_2): 2138m, 2054vs, 2006s, 1662s, 1634m, 1606m cm^{-1}. ^{1}H NMR: 7.2–7.8 broad multiplet, CD_2Cl_2.

A reaction between $MnBr(CO)_5$ and PPN[phth] in a 1/2 ratio (CH_2Cl_2, 2 h, work-up as above) yields $PPN[Mn(CO)_4(phth)_2]$ in 45% yield. Similarly, the reaction between $Mn_2(\mu\text{-}Br)_2(CO)_8$ and PPN[phth] (1 Mn to 2 phth$^-$) gave this species as the only organometallic product.

A small amount of $Mn(CO)_5(phth)$ was isolated from a 1/1 reaction of $[Mn(CO)_5(MeCN)]PF_6$ and PPN[phth] (CH_2Cl_2, 1 h, 22°C).

Other reactions

A solution containing $Mn(SPh)(CO)_5$ (also containing [PPN]SPh) was prepared by the reaction of $PPN[Mn(CO)_5]$ and PhSSPh [2] in CH_2Cl_2 at −78°C. One equivalent of PhSphth was added to the solution at this temperature. After 2.5 h at −78°C the solution was warmed to room temperature. Workup of the reaction mixture provided a mixture of $PPN[Mn(CO)_4(phth)_2]$ and $PPN[Mn_2(\mu\text{-}SPh)_3(CO)_6]$. We suspect that PhSphth reacted initially with [PPN]SPh to give PPN[phth] and PhSSPh and the former species then reacts with $Mn(SPh)(CO)_5$ to

give PPN[Mn(CO)$_4$(SPh)(phth)]. This intermediate would then disproportionate to the observed product, as noted above.

A mixture of PPN[Mn(CO)$_4$(phth)$_2$] and PPN[Mn$_2$(μ-SPh)$_3$(CO)$_6$] was similarly obtained by reaction of Mn(SPh)(CO)$_5$, prepared in situ as described above and in ref. 2, and PPN[phth] in a 1/1 molar ratio.

Reaction of PPN[Mn(CO)$_4$(phth)$_2$] and HCl. Concentrated aqueous HCl (2.0 ml) was added to a solution of PPN[Mn(CO)$_4$(phth)$_2$] (0.1 g, 0.1 mmol) in 20 ml acetone. After a few minutes, the solvent was removed using a stream of N$_2$. The residue, whose infrared spectrum showed bands due to phthH and PPN[Mn$_2$(μ-Cl)$_3$(CO)$_6$], was recrystallized from CH$_2$Cl$_2$/Et$_2$O giving the known organometallic product [13] in 58% yield.

Reaction of PPN[CpMo(CO)$_3$] and PhSphth. A solution of PhSphth (0.10 g, 0.39 mmol) in 10 ml CH$_2$Cl$_2$ was added to a solution of PPN[CpMo(CO)$_3$] (0.15 g, 0.19 mmol) in 40 ml CH$_2$Cl$_2$ at room temperature. An infrared spectrum run immediately ($\sim$ 1 min) indicated complete conversion to CpMo(CO)$_3$SPh (ν(CO) 2041s, 1951s, br cm^{-1}; [2]). Over the next 90 min, these absorptions decrease in intensity concurrent with an increase in intensity of absorptions at 1949s, 1831s, and 1654s cm^{-1}. The first two ν(CO) values coincide closely with ν(CO) values for known [CpMo(CO)$_2$(X)$_2$]$^-$ species [14]. Attempts to isolate this complex were unsuccessful, due to its apparent low stability. It may be noted that the halide complexes of this formula were also not isolated.

Crystal structure determination of PPN[Mn(CO)$_4$(phth)$_2$]

Well formed yellow crystals suitable for X-ray analysis were obtained by vapor diffusion of hexane into a CH$_2$Cl$_2$ solution of the compound at 295 K.

C$_{56}$H$_{38}$MnN$_3$O$_8$P$_2$; mol. wt. 997.8; monoclinic a 9.189(3), b 20.563(12), c 26.258(11) Å, β 93.16(3)$^\circ$; U 4954 Å^3; 293 K; $Z = 4$, D_c 1.34 g cm^{-3}; $F(000) = 2056$; λ(Mo-K_α) 0.71073 Å; μ(Mo-K_α) 3.42 cm^{-1}; space group $P2_1/n$ (No. 14); $R = 0.063$ for 4218 unique observed reflections.

A single crystal (yellow parallelepiped, $\sim$ 0.2 $\times$ 0.25 $\times$ 0.5 mm) was mounted on a glass fiber with cyanoacrylate glue. Preliminary examination of the crystal on a Nicolet P3/F four-circle diffractometer established a four-molecule monoclinic unit cell. Procedures for operations carried out on the diffractometer are similar to those described elsewhere [15,16]. The orientation matrix and unit cell parameters were determined from a least squares refinement based on the setting angles of 25 accurately centered reflections from diverse regions of reciprocal space (12° $\leq 2\theta \leq$ 30°). The centrosymmetric space group, $P2_1/n$ was uniquely determined by the systematic absences: $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$.

The same crystal used for preliminary characterization was utilized for data collection. The data (2θ 4.0–50.66; sinθ/λ_{max} 0.602 Å^{-1}; 9052 unique) from the octants hkl and $-hkl$ were collected with graphite-monochromated Mo-K_α X-radiation (the θ-2θ planes of the monochromator and the diffractometer were parallel) using 96 step ω scans each with a total scan range of 0.8° equally distributed about the peak center. The scan rate was variable and ranged from 5.0 to 29.3°/min based on the intensity of a 2 s prescan through the peak. Backgrounds were extracted from the peak profiles using the local program CARESS which incorporates the Lehman–Larson algorithms [17]. Throughout the data collection four standard reflections from diverse regions of reciprocal space were monitored every 100

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND ISOTROPIC THERMAL PARAMETERS ($\text{Å}^2 \times 10^3$) FOR PPN[Mn(CO)$_4$(phth)$_2$]

	x	y	z	U^a
Mn	4779(1)	7176(1)	45(1)	41(1)
C(1)	3466(7)	7053(3)	−525(2)	47(2)
O(1)	2581(5)	6937(2)	−827(2)	63(2)
C(2)	5235(7)	6330(3)	28(2)	56(2)
O(2)	5534(5)	5787(2)	13(2)	87(2)
C(3)	3302(7)	7024(3)	453(2)	55(3)
O(3)	2390(6)	6929(3)	717(2)	97(2)
C(4)	6001(7)	7256(3)	629(2)	53(2)
O(4)	6676(5)	7217(2)	1000(2)	83(2)
N(1)	4266(5)	8139(2)	39(2)	38(2)
C(5)	3876(6)	8511(3)	−390(2)	42(2)
O(5)	3864(5)	8322(2)	−833(1)	61(2)
C(6)	3417(7)	9167(3)	−222(2)	54(2)
C(7)	2928(9)	9700(4)	−490(3)	89(4)
C(8)	2634(10)	10254(4)	−200(3)	103(4)
C(9)	2808(11)	10260(4)	321(3)	110(4)
C(10)	3312(8)	9719(3)	580(3)	83(3)
C(11)	3591(7)	9174(3)	296(2)	54(2)
C(12)	4131(6)	8522(3)	462(2)	49(2)
O(12)	4400(5)	8348(2)	901(2)	73(2)
N(2)	6441(4)	7401(2)	−408(2)	38(2)
C(13)	6557(6)	7178(3)	−900(2)	43(2)
O(13)	5781(5)	6777(2)	−1111(2)	63(2)
C(14)	7833(7)	7495(3)	−1116(2)	48(2)
C(15)	8415(8)	7449(4)	−1593(3)	71(3)
C(16)	9574(10)	7797(4)	−1670(4)	94(4)
C(17)	10300(9)	8181(5)	−1292(4)	97(4)
C(18)	9727(7)	8237(4)	−823(3)	74(3)
C(19)	8483(6)	7893(3)	−743(2)	54(2)
C(20)	7582(6)	7824(3)	−288(2)	47(2)
O(20)	7841(5)	8091(2)	123(2)	71(2)
N(3)	8601(5)	4358(2)	2041(2)	40(2)
P(1)	8221(2)	4893(1)	1618(1)	35(1)
C(21)	6315(6)	5111(3)	1544(2)	35(2)
C(22)	5807(7)	5727(3)	1652(2)	47(2)
C(23)	4334(7)	5865(3)	1584(2)	58(3)
C(24)	3387(7)	5391(4)	1409(2)	62(3)
C(25)	3887(7)	4780(3)	1311(3)	64(3)
C(26)	5348(7)	4639(3)	1376(2)	51(2)
C(27)	9262(6)	5623(2)	1737(2)	37(2)
C(28)	10200(6)	5673(3)	2169(2)	52(2)
C(29)	10995(7)	6234(3)	2262(3)	66(3)
C(30)	10847(8)	6746(4)	1933(3)	70(3)
C(31)	9942(8)	6705(3)	1502(3)	70(3)
C(32)	9137(6)	6141(3)	1402(2)	51(2)
C(33)	8726(6)	4582(3)	1014(2)	35(2)
C(34)	9952(6)	4187(3)	998(2)	47(2)
C(35)	10393(7)	3954(3)	540(3)	60(3)
C(36)	9609(8)	4097(3)	97(3)	61(3)
C(37)	8394(8)	4485(3)	104(2)	60(3)
C(38)	7953(7)	4734(3)	563(2)	49(2)
P(2)	7979(2)	4153(1)	2566(1)	37(1)

TABLE 1 (continued)

	x	y	z	U^a
C(39)	6886(6)	3426(2)	2501(2)	34(2)
C(40)	6893(6)	3067(3)	2057(2)	44(2)
C(41)	6116(7)	2496(3)	2011(2)	58(3)
C(42)	5335(7)	2282(3)	2407(2)	56(2)
C(43)	5342(7)	2635(3)	2857(2)	53(2)
C(44)	6116(6)	3202(3)	2906(2)	47(2)
C(45)	6899(7)	4759(3)	2863(2)	38(2)
C(46)	7567(7)	5276(3)	3125(2)	57(3)
C(47)	6750(11)	5759(3)	3324(3)	73(3)
C(48)	5245(11)	5735(4)	3269(3)	78(4)
C(49)	4569(8)	5243(4)	3000(3)	73(3)
C(50)	5394(7)	4753(3)	2797(2)	51(2)
C(51)	9494(6)	3966(3)	3004(2)	45(2)
C(52)	9290(8)	3825(3)	3511(2)	72(3)
C(53)	10443(10)	3647(4)	3832(3)	92(4)
C(54)	11802(10)	3610(4)	3660(4)	87(4)
C(55)	12042(8)	3735(4)	3156(4)	90(4)
C(56)	10871(7)	3913(3)	2822(3)	71(3)

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

reflections. The intensities of the standard reflections showed no systematic variations during the time required to collect the data.

Intensities and standard deviations were calculated using the formulas given previously [18]. Lorentz and polarization [19] corrections were then applied to I and $\sigma(I)$. The formula used for polarization assumed the monochromator crystal was 50% ideally mosaic and 50% ideally perfect. Empirical absorption corrections [20] were applied (μ(Mo-K_α) 3.42 cm^{-1}). The data with $F_0 > 3\sigma(F_0)$ were retained as observed, leading to 4218 reflections (47% of the theoretical number possible for sin θ/λ < 0.602 Å^{-1}) that were used for the refinement of the structure.

Initial phasing information was obtained by direct methods and the rest of the non-hydrogen atoms were located by standard Fourier techniques. The resulting model was refined to convergence assuming isotropic thermal motion for all atoms, after which the hydrogen atoms were included in calculated idealized positions (d(C–H) 0.96 Å) as fixed contributors. The model was then refined allowing the non-hydrogen atoms to vibrate anisotropically. Solution and refinement were carried out using the SHELXTL [20] package. Standard values for the atomic scattering factors, including corrections for anomalous dispersion, were employed throughout the structure analysis [21].

Least-squares refinement of this model converged with discrepancy indices $R_1 = \Sigma\|F_o\| - \|F_c\|\|/\Sigma|F_o| = 0.063$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2} = 0.061$. The estimated error in an observation of unit weight was 1.019 and the highest residual on the difference electron density Fourier map was 0.36 e/Å^3. Fractional monoclinic coordinates and selected interatomic distances and angles are given in Tables 1 and 2. Anisotropic thermal parameters, more complete distance and angle lists, coordinate positions for the fixed hydrogen contributors, and a listing of $10|F_0|$, $10|F_c|$, and $10\sigma(F_o)$ are included as supplementary material (59 pages).

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR PPN[Mn(CO)$_4$(phth)$_2$]

Mn–C(1)	1.888(6)	Mn–C(2)	1.790(6)
Mn–C(3)	1.802(7)	Mn–C(4)	1.857(6)
Mn–N(1)	2.037(4)	Mn–N(2)	2.041(4)
C(1)–O(1)	1.130(7)	C(2)–O(2)	1.151(7)
C(3)–O(3)	1.133(8)	C(4)–O(4)	1.129(7)
N(1)–C(5)	1.393(6)	N(1)–C(12)	1.372(7)
C(5)–O(5)	1.226(6)	C(5)–C(6)	1.487(8)
C(6)–C(7)	1.365(9)	C(6)–C(11)	1.362(8)
C(7)–C(8)	1.405(11)	C(8)–C(9)	1.369(12)
C(9)–C(10)	1.371(11)	C(10)–C(11)	1.377(9)
C(11)–C(12)	1.486(8)	C(12)–O(12)	1.219(6)
N(2)–C(13)	1.379(7)	N(2)–C(20)	1.385(7)
C(13)–O(13)	1.206(7)	C(13)–C(14)	1.480(8)
C(14)–C(15)	1.392(9)	C(14)–C(19)	1.386(8)
C(15)–C(16)	1.384(12)	C(16)–C(17)	1.369(13)
C(17)–C(18)	1.369(12)	C(18)–C(19)	1.370(9)
C(19)–C(20)	1.498(8)	C(20)–O(20)	1.221(7)
N(3)–P(1)	1.587(4)	N(3)–P(2)	1.579(4)
P(1)–C(21)	1.808(6)	P(1)–C(27)	1.799(5)
P(1)–C(33)	1.795(5)	P(2)–C(39)	1.802(5)
P(2)–C(45)	1.799(6)	P(2)–C(51)	1.797(6)
C(1)–Mn–C(2)	89.5(3)	C(1)–Mn–C(3)	88.8(3)
C(2)–Mn–C(3)	91.8(3)	C(1)–Mn–C(4)	176.2(3)
C(2)–Mn–C(4)	88.5(3)	C(3)–Mn–C(4)	88.0(3)
C(1)–Mn–N(1)	89.2(2)	C(2)–Mn–N(1)	178.1(2)
C(3)–Mn–N(1)	89.5(2)	C(4)–Mn–N(1)	92.9(2)
C(1)–Mn–N(2)	91.9(2)	C(2)–Mn–N(2)	91.3(2)
C(3)–Mn–N(2)	176.8(2)	C(4)–Mn–N(2)	91.4(2)
N(1)–Mn–N(2)	87.4(2)	Mn–C(1)–O(1)	171.5(5)
Mn–C(2)–O(2)	179.3(5)	Mn–C(3)–O(3)	178.7(6)
Mn–C(4)–O(4)	170.1(6)	Mn–N(1)–C(5)	126.2(3)
Mn–N(1)–C(12)	125.6(3)	Mn–N(2)–C(13)	124.7(3)
Mn–N(2)–C(20)	126.2(4)	P(1)–N(3)–P(2)	136.1(3)
N(3)–P(1)–C(21)	114.9(2)	N(3)–P(1)–C(27)	111.3(2)
C(21)–P(1)–C(27)	108.3(2)	N(3)–P(1)–C(33)	108.3(2)
C(21)–P(1)–C(33)	106.8(2)	C(27)–P(1)–C(33)	106.8(3)
N(3)–P(2)–C(39)	111.5(2)	N(3)–P(2)–C(45)	115.3(2)
C(39)–P(2)–C(45)	107.3(3)	N(3)–P(2)–C(51)	108.1(3)
C(39)–P(2)–C(51)	106.9(2)	C(45)–P(2)–C(51)	107.3(3)

Discussion

The reaction between PPN[CpW(CO)$_3$] and PhSphth occurred upon mixing dichloromethane solutions of these reagents, (eq. 1). Workup of the reaction provided a good yield of the product, CpW(CO)$_3$SPh, a red crystalline solid which had been prepared previously by another route [11]. As noted earlier, this is the "expected" product based on the known reactivity of PhSphth.

$$PPN[CpW(CO)_3] + PhSphth \rightarrow CpW(CO)_3SPh + PPN[phth] \tag{1}$$
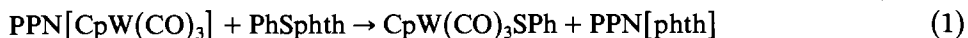
One might consider this an example of a "good" synthetic procedure for metal thiolate species, in view of the minimal difficulty of the experimental procedure and

the yield of product. Arguing against this is the fact that the synthesis of the precursor, PhSphth, adds a substantial time increment to the procedure. However, a more interesting limitation was encountered when attempts were made to generalize this procedure by extending it to other metal carbonyl systems, as described below.
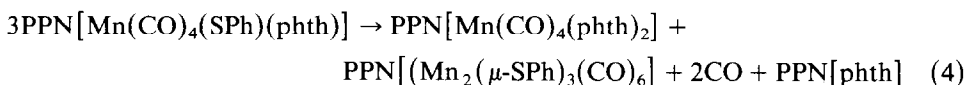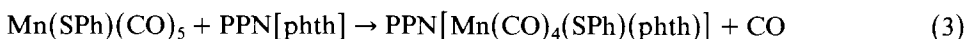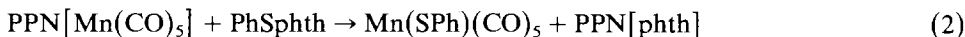
The products of the $PPN[Mn(CO)_5]$/PhSphth reaction are dependent on reaction stoichiometry, with the 1/2 reaction easiest to describe. This reaction occurs rapidly in CH_2Cl_2, even at $-26°C$. As expected, $Mn(SPh)(CO)_5$ is the initial product; this species is identified in situ by characteristic $\nu(CO)$ absorptions at 2126, 2038, and 2008 cm^{-1} [2]. However, the spectrum of the solution changes rapidly; these absorptions disappear and are replaced in a few minutes by new absorptions for an intermediate **A** at 2075w, 1997vs, 1972s, 1923s, 1915 vs cm^{-1}. On further standing at $-26°C$ for 4 h, the spectrum evolves further to give the infrared pattern of the final product with $\nu(CO)$ values at 2090w, 2004s, 1980vs, 1928s cm^{-1}. Warming to room temperature and evaporation of the solvent gives a yellow residue purified by column chromatography. Analyses, spectroscopic data, and a crystal structure lead to identification of this species as $PPN[Mn(CO)_4(phth)_2]$.

The same (1/2) reaction run at room temperature is complete in several minutes, giving $PPN[Mn(CO)_4(phth)_2]$ in 50% isolated yield; this is the only organometallic product present according to infrared evidence.

A 1/1 reaction of $PPN[Mn(CO)_5]$ and PhSphth followed the same initial steps giving first $Mn(SPh)(CO)_5$ followed by rapid conversion of this species to intermediate **A** (as in the 1/2 reaction). At this point the stoichiometry should be expected to limit the further reaction, since no additional phthalimide anion is available. However, there is conversion to $PPN[Mn(CO)_4(phth)_2]$, accompanied by the formation of a second species, $PPN[Mn_2(\mu\text{-}SPh)_3(CO)_6]$. Separation of the mixture of these two ionic products can be accomplished with difficulty by crystallization.

The initially formed reagent $Mn(SPh)(CO)_5$ obviously reacts further with the phthalimide ion in this solution. It is known that $Mn(SPh)(CO)_5$ readily loses carbon monoxide, forming dimeric $Mn_2(\mu\text{-}SPh)_2(CO)_8$ when there is no other reagent present [2]. However, this dimer is not detected among the products, which means that the 16e intermediate formed by CO loss from $Mn(SPh)(CO)_5$ must be intercepted by the phthalimide ion. This would lead to identification of **A** as $PPN[Mn(CO)_4(SPh)(phth)]$. The infrared spectrum containing four $\nu(CO)$ absorptions at slightly lower frequencies than the absorptions seen for $PPN[Mn(CO)_4\text{-}(phth)_2]$ is in accord with the assumption that PhS is a poorer electron acceptor than the phthalimide ligand. Apparently $PPN[Mn(CO)_4(SPh)(phth)]$ is unstable with respect to ligand redistribution since $PPN[Mn(CO)_4(phth)_2]$ is a product of the 1/1 reaction. The other product should be $PPN[Mn(CO)_4(SPh)_2]$. However this species is not known; numerous attempts to make salts of this anion led instead to salts of $[Mn_2(\mu\text{-}SPh)_3(CO)_6]^-$ [2,12].

This reaction pathway is summarized in the series of equations below:

$$PPN[Mn(CO)_5] + PhSphth \rightarrow Mn(SPh)(CO)_5 + PPN[phth] \qquad (2)$$

$$Mn(SPh)(CO)_5 + PPN[phth] \rightarrow PPN[Mn(CO)_4(SPh)(phth)] + CO \qquad (3)$$

$$3PPN[Mn(CO)_4(SPh)(phth)] \rightarrow PPN[Mn(CO)_4(phth)_2] +$$

$$PPN[(Mn_2(\mu\text{-}SPh)_3(CO)_6] + 2CO + PPN[phth] \qquad (4)$$

In the reaction between PPN[Mn(CO)$_5$] and PhSphth in a 1/2 ratio, PPN[Mn(CO)$_4$(phth)$_2$] is the only organometallic product formed. The second equivalent of PhSphth must react with the intermediate PPN[Mn(CO)$_4$(SPh)(phth)] in a manner that formally involved combining PhS$^-$ (from this species) with PhS$^+$ (from PhSphth). The net result is to form PhSSPh as well as PPN[Mn(CO)$_4$(phth)$_2$], tying up the thiolate groups and preventing their incorporation into an isolable organometallic product.

Following the inadvertent synthesis of PPN[Mn(CO)$_4$(phth)$_2$] in these reactions, we showed that these species could also be prepared in a predictable fashion from either MnBr(CO)$_5$ or Mn$_2$(μ-Br)$_2$(CO)$_8$ and PPN[phth] using appropriate stoichiometries of these reactants. The synthesis of Mn(CO)$_5$(phth) was accomplished by reactions of MnBr(CO)$_5$ or [Mn(CO)$_5$(MeCN)]PF$_6$ with PPN[phth] using a 1/1 molar ratio. The reaction between PPN[Mn(CO)$_4$(phth)$_2$] and HCl(aq) giving PPN[Mn$_2$(μ-Cl)$_3$(CO)$_6$], a known complex [13], was also demonstrated.

Results similar to those encountered in the manganese system were also seen in the PPN[CpMo(CO)$_3$]/PhSphth reaction. Initially CpMo(CO)$_3$SPh is formed but a further reaction ensues with a second equivalent of PhSphth to give a species believed to be PPN[CpMo(CO)$_2$(phth)$_2$]. In the infrared spectrum ν(CO) values are quite similar to values given in the literature for [CpMo(CO)$_2$X$_2$]$^-$ (X = Cl, Br, I) [14]. Like the halide complexes, the phthalimide complex is unstable and could not be isolated.

There are several references to organometallic complexes containing phthalimide ligands. Reactions between the phthalimide anion and either M(CO)$_6$ or M(CO)$_5$(THF) [22], or between the anion of hydroxyphthalimide and M(CO)$_6$ [23], yield anionic complexes [M(CO)$_5$(phth)]$^-$ (M = Cr, Mo, W), isolated as tetraphenylarsonium salts. The phthalimide anion replaces chloride ion in CpW(CO)$_3$Cl to form CpW(CO)$_3$(phth) [23]. As noted earlier phthalimide platinum complexes are formed by oxidative addition of phthSSR to a platinum(0) precursor [3]. Numerous references exist to non-organometallic coordination compounds with this ligand group [24].

The complex PPN[Mn(CO)$_4$(phth)$_2$] is a yellow crystalline solid. Its ν(CO) values 2090w, 2004s, 1980ms, 1928s cm^{-1} (in CH$_2$Cl$_2$) are quite similar to ν(CO) values of other [MnX$_2$(CO)$_4$]$^-$ species (X = Cl, Br, I [25], CN [26]); for example ν(CO) values for Et$_4$N[MnI$_2$(CO)$_4$] are at 2082m, 2006s, 1986s, and 1939s cm^{-1} (in C$_2$H$_4$Cl$_2$) [25]. Likewise, the ν(CO) values for orange Mn(CO)$_5$(phth) (2138m, 2054s, and 2006s cm^{-1}) and MnCl(CO)$_5$ (2138w, 2053vs, and 2001s cm^{-1}) [27] are similar. These data suggest that the phthalimide ligand is quite like halide ion in its electron donor–acceptor ability.

Stretching frequencies associated with the phthalimide ligand are located at 1649vs, 1625vs, and 1607s cm^{-1} (for PPN[Mn(CO)$_4$(phth)$_2$]) and at 1662s, 1634m, and 1606m cm^{-1} (for Mn(CO)$_5$(phth)). These values are somewhat lower than values quoted for other organometallic complexes with phthalimide ligands: for example, the complex Ph$_4$As[W(CO)$_5$(phth)] is reported to have absorptions at 1720 and 1640 cm^{-1}, while CpW(CO)$_3$(phth) values are 1739, 1663, and 1631 cm^{-1} [22,23]. Lacking clear assignments for these vibrational frequencies, we cannot rationalize these values.

The structure of PPN[Mn(CO)$_4$(phth)$_2$], determined by single crystal X-ray diffraction techniques, consists of discrete cations and anions. The structure of the

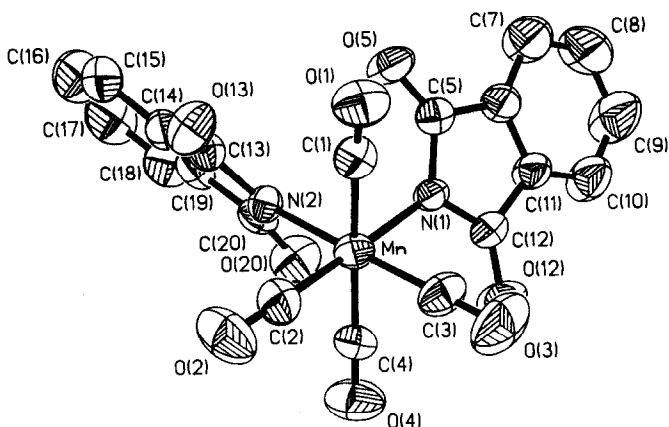Fig. 1. Structure of the anion [Mn(CO)₄(phth)₂]⁻.

anion is given in Fig. 1, and selected bond length and bond angle information are assembled in Table 1. The overall structure has an octahedral geometry at manganese with the phthalimido-ligands in *cis* positions. Each Mn-phthalimide unit is planar with the phthalimide planes tilted at 57.1 and 67.1° relative to equatorial planes containing manganese, N_1 and N_2 of these ligands and the carbons C(2) and C(3) in the carbonyl groups. The two carbonyls perpendicular to this plane deviate somewhat from linearity, with M–C–O angles of 169.8 and 171.7°. These values are most likely set to minimize steric interactions in these systems. The two carbon–manganese bonds *trans* to the phthalimide ligands are very slightly longer than the other two manganese–carbon bonds. The bond lengths parameters for the phthalimido ligand appear to be similar to values for *cis*-Pt(PPh₃)₂(phth)(SSPrⁱ) whose crystal structure was determined [3] and to the parameters of other organic phthalimido compounds [28].

References

1 B.M. Trost and S.J. Martin, J. Am. Chem. Soc., 106 (1984) 4263; and cited references.
2 P.M. Treichel and P.C. Nakagaki, Organometallics, 5 (1986) 711.
3 A. Shaver, J. Hartgerink, R.D. Lai, P. Bird and N. Ansari, Organometallics, 2 (1983) 938.
4 A. Shaver, J.M. McCall, P.H. Bird and N. Ansari, Organometallics, 2, (1983) 1894.
5 D.L. Nosco, R.C. Elder and E. Deutsch, Inorg. Chem., 19 (1980) 2545.
6 M. Behforouz and J.E. Kerwood, J. Org. Chem., 34 (1969) 51.
7 K. Inkrott, G. Goetze and S.G. Shore, J. Organomet. Chem., 154 (1978) 337
8 R.B. King, Organometallic Syntheses, Vol. 1, Academic Press, New York, 1965, p. 174.
9 F. Zingales and V. Sartorelli, Inorg. Chem., 6 (1967) 1243.
10 D. Drew, D.J. Darensbourg and M.Y. Darensbourg, Inorg. Chem., 14 (1975) 1579.
11 H.B. Abrahamson and M.L. Freeman, Organometallics, 2 (1983) 679.
12 P.M. Treichel and M.H. Tegen, J. Organomet. Chem., 292 (1985) 385.
13 J.L. Cihonski, M.L. Walker and R.A. Leverson, J. Organomet. Chem., 102 (1975) 335.
14 A.R. Burkett, T.J. Meyer and D.G. Whitten, J. Organomet. Chem., 67 (1974) 67; J.L. Hughey and T.J. Meyer, Inorg. Chem., 14 (1975) 947.
15 Data Collection Operation Manual. Nicolet X-Ray Instruments: Madison, WI (1985).
16 Nicolet Crystallographic Systems User's Guide, Nicolet X-Ray Instruments: Madison, WI 1985.
17 R. Blessing, P. Coppens, and P. Becker, J. Appl. Crystallog., 7 (1974) 488: M.S. Lehmann and F.K. Larson, Acta Crystallogr., A, 30 (1974) 580.

18 K.J. Haller and J.H. Enemark, Inorg. Chem., 17 (1978) 3552.

19 K.A. Kerr and J.P. Ashmore, Acta Crystallogr., A, 30 (1974) 176.

20 SHELXTI, Nicolet X-Ray Instruments, Madison, WI, 1985.

21 Atomic form factors from: D.T. Cromer and J.B. Mann, International Tables for X-Ray Crystallography, Kynoch Press: Birmingham, UK, 1974, Vol. IV, 99–101, Table 2.2B. The atomic form factor for hydrogen from: R.F. Stewart, E.R. Davidson, W.T. Simpson, J. Chem. Phys., 42 (1965) 3175. Anomalous scattering components from: D.T. Cromer, D. Liberman, J. Chem. Phys., 53 (1970) 1891.

22 W. Beck and E. Schier, Z. Naturforsch. B, 25 (1970) 221.

23 W. Beck, F. Gotzfried, and E. Schier, J. Organomet. Chem., 150 (1978) 247.

24 See G. Narain, J. Inorg. Nucl. Chem., 28 (1968) 2403; Can. J. Chem., 44 (1966) 975; and G. Narain and P.R. Shukla, Aust. J. Chem., 20 (1967) 227.

25 R.J. Angelici, Inorg. Chem., 3 (1964) 1099.

26 W. Hieber and W.K. Schropp, Z. Naturforsch. B, 14 (1959) 460.

27 H.D. Kaesz, R. Bau, D. Hendrickson and J.M. Smith, J. Am. Chem. Soc., 89 (1967) 2844.