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TRISPHAT Anion. An Efficient NMR Chiral Shift Counterion for Cationic Tricarbonyl Manganese Complexes with Planar Chirality

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Summary: The determination of the enantiomeric purity of chiral $Mn(CO)_3$ complexes of substituted anisoles and toluenes is conveniently carried out by ^1H NMR analysis after anion exchange with TRISPHAT, the chiral anion behaving as a diamagnetic chiral shift reagent.

Introduction

Cationic (η^6-arene)manganese complexes are very important and versatile synthetic intermediates in organometallic and organic chemistry.[1] However, they have found less applications than the related neutral (η^6-arene)chromium complexes. Whereas the chromium complexes were successfully used in a wide range of applications in stereoselective reactions,[1c,2] only a few examples of asymmetric syntheses using cationic manganese complexes have been reported, up to now. The latter complexes allow an access, for example, to enantiopure natural products[3] as well as pharmaceutically important antiinflammatory agents.[4] All these syntheses involve addition of enantiopure nucleophiles to chiral racemic electrophilic (arene)manganese complexes. Although it has been reported the preparation of enantiopure chromium complexes[5] as well as the elaboration of efficient NMR tools to determine the enantiomeric purity of chiral Cr complexes,[6] no study has been yet reported concerning chiral manganese complexes. Thus, in the course of our research in the field of Cr and Mn complexes-mediated organic syntheses,[1d,7] we were interested in the elaboration of an efficient technique for the determination of the enantiomeric purity of tricarbonylmanganese complexes with planar chirality.

Recently, it has been shown that readily prepared and resolved tris(tetrachlorobenzenediolato)phosphate(V) anion **1** (TRISPHAT) is configurationally stable in solution as an ammonium salt, e.g., [cinchonidinium][Δ-**1**].[8] This anion is a useful diamagnetic NMR chiral shift reagent for cationic transition metal complexes and phosphonium salts.[9,10] The efficiency of the reagent was explained by the formation—in low polar solvent media—of diastereomeric contact ion pairs between the anion **1** and the chiral cations. The resulting short-range diastereomeric interactions lead to a nonequivalence for the enantiomers of the cations. Lately, we have shown that TRISPHAT is also an effective NMR chiral shift

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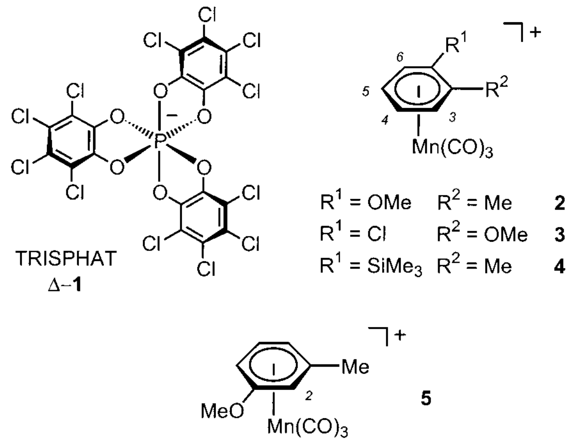

Figure 1. TRISPHAT anion (**1**) and arene $Mn(CO)_3$ complexes (**2**−**5**).

agent for neutral $Cr(CO)_3$ complexes of substituted benzaldehydes and nitrones with planar chirality.[6c] The efficiency was then explained by strong charge-dipole interactions allowing a differentiation of the two enantiomers.

Cationic tricarbonyl manganese complexes cannot, however, be prepared from benzaldehydes and nitrones.[11] Arenes substituted with functional groups such as Cl, OMe, $SiMe_3$ (TMS)—of weak dipole moments—can only be used for their preparation by direct complexation to the $Mn(CO)_3$ fragment. The resulting cationic $Mn(CO)_3$ complexes are poorly soluble in solvents such as C_6D_6 or CD_2Cl_2. Polar solvents, e.g., acetone, are thus necessary to dissolve the complexes for ^{1}H NMR analysis. It was then debatable—in rather polar solvent conditions and in the absence of strong charge-dipole interactions—whether the Coulombic attraction would be sufficiently strong for anion **1** to behave as an NMR chiral shift reagent for cationic $Mn(CO)_3$ complexes with planar chirality. This is indeed the case, and we report here that the enantiomeric purity of arene $Mn(CO)_3$ complexes can be determined by using the TRISPHAT anion once the [(arene)Mn(CO)$_3$][TRISPHAT] ion pairs have been prepared prior to the analysis.

Results and Discussion

The chiral (arene)tricarbonylmanganese complexes **2**−**5** were prepared as racemic mixtures by the reaction of the appropriate arenes with the in situ generated [$Mn(CO)_5$][BF_4] or a mixture of $BrMn(CO)_5$ and $AlCl_3$.[12]

Initial experiments to determine the efficiency of the TRISPHAT anion as an NMR chiral shift agent were attempted following conditions reported for the $Cr(CO)_3$ complexes.[6c] Racemic (arene)tricarbonylmanganese derivatives [**2**−**4**][BF_4] and [**5**][PF_6] (Figure 1) were studied and, as foreseen, salts [**2**,**3**][BF_4] and [**5**][PF_6] proved to be insoluble in most solvents or solvent combinations of low polarity. Only salt [**4**][BF_4] could be dissolved in decent amounts in 20% acetone-d_6/C_6D_6, the other derivatives being barely soluble in this solvent mixture. We therefore tested the protocol developed for the $Cr(CO)_3$ complexes on a solution of salt [**4**][BF_4] in 20% acetone-d_6/C_6D_6.[13] In an NMR tube, [n-Bu_4N][Δ-**1**] was added as a solid, and a poor separation of the signals ($\Delta\delta$) of the enantiomers of **4** resulted from the addition (Figure 2).[14] It was necessary to add at least 2.9 equiv of the reagent to observe the beginning of a good nonequivalence of the signals, and even with 11.7 equiv of the shift reagent, baseline-to-baseline separations could not be realized. More importantly, it was essential to filter the solution of salts [**4**][BF_4] and [n-Bu_4N][Δ-**1**] over Celite prior to the ^{1}H NMR analysis. Otherwise, a low resolution was observed due to the appearance of broad signals (e.g., Figure 2, spectrum b). This set of results being disappointing, we looked for an alternative procedure using chiral anion **1** as NMR chiral shift agent.

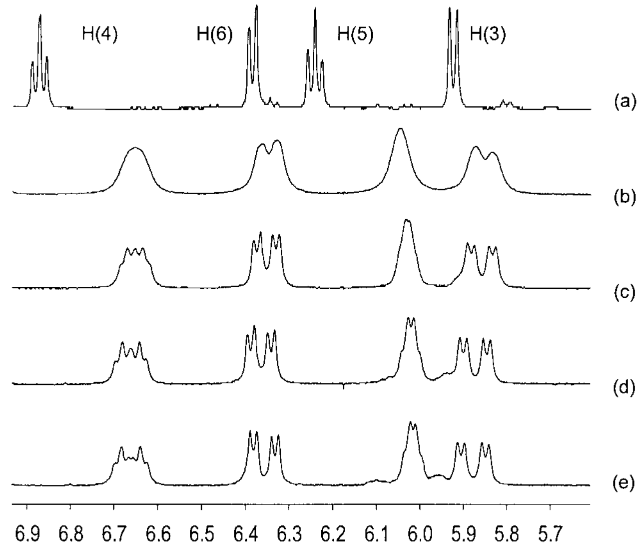

Figure 2. ^{1}H NMR spectra (parts, 400 MHz) of [**4**][BF_4] in C_6D_6/20% acetone-d_6 with various quantities of [n-Bu_4N][Δ-**1**]: (a) 0 equiv, (b) 2.0 equiv, (c) 2.9 equiv, (d) 5.7 equiv, and (e) 11.7 equiv; for spectra (a), (c), (d), and (e), solutions are filtered over Celite prior to analysis.

Recently, we have observed that the TRISPHAT anion confers to its salts an affinity for low polar organic solvents, and once dissolved in $CHCl_3$ or CH_2Cl_2, they do not partition in aqueous layers and elute very rapidly on chromatography over silica gel/alumina.[9b,15] We therefore considered the preparation of the TRISPHAT salts of the $Mn(CO)_3$ complexes **2**−**5**, expecting that the increased lipophilicity of the ion pairs would allow us to dissolve them in less polar NMR solvents, and this would then result in a better separation of the NMR signals of the enantiomers.

(11) We have recently reported a two-step preparation of cationic (η^6-arene)$Mn(CO)_3$ substituted by electron-withdrawing groups such as ketone, ester, or amide. Auffrant, A.; Prim, D.; Rose-Munch, F.; Rose, E. *Organometallics*, submitted. However, the preparation of cationic manganese complexes substituted by aldehyde groups has not been described so far.

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(13) DMSO—initially tried as a cosolvent for the solubilization of the cationic (η^6-arene)$Mn(CO)_3$—cannot be used, as decomplexation is observed.

(14) As no hydrogen atom is present on the anion, a rather large ^{1}H NMR spectral window (δ > 3.2 ppm) is available for the analyses with [n-Bu_4N][Δ-**1**].

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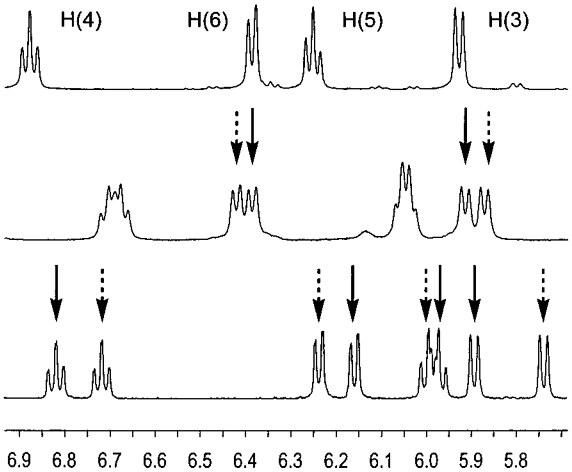

Figure 3. ^{1}H NMR spectra (parts, 400 MHz) of (a) [**4**][BF_4] in 20% acetone-d_6/C_6D_6 and of [**4**][Δ-**1**] in (b) 20% acetone-d_6/C_6D_6 and (c) 5% acetone-d_6/C_6D_6, respectively. The plain and broken arrows correspond to each enantiomer.

For the preparation of the TRISPHAT salts, solutions in acetone of [cinchonidinium][Δ-**1**] and of [rac-**2**−**4**][BF_4] or [rac-**5**][PF_6] were prepared and mixed together.[16] Aliquots were adsorbed on analytical basic alumina plates. Development by elution with CH_2Cl_2 showed as expected a much-reduced affinity of salts [**2**−**5**][Δ-**1**] for basic alumina, as they were retained to a much lower extent (R_f 0.26 to 0.88) than their BF_4 or PF_6 precursors (R_f ~0).[15c] Preparative column chromatography experiments (Al_2O_3, pH (aqueous suspension): 9.5 ± 0.5, CH_2Cl_2, 1.0 × 0.5 cm) using mixtures of [cinchonidinium][Δ-**1**] (1.2 equiv, ~60 μmol) and of [rac-**2**−**4**][BF_4] or [rac-**5**][PF_6] (~50 μmol) were performed, and the resulting [rac-**2**−**5**][Δ-**1**] salts were isolated in modest to decent yields (26−63%). As foreseen, the TRISPHAT salts exhibited a higher solubility in low polar solvent conditions and could be dissolved in either 5% or 20% acetone-d_6/C_6D_6. ^{1}H NMR analysis of the isolated [**2**−**5**][Δ-**1**] salts confirmed our prediction. The signals of both enantiomers of the cations could be observed in a 1:1 ratio in 5% acetone-d_6/C_6D_6 (Figures 3 and 4).[17] For the cationic chiral $Mn(CO)_3$ **2**−**5**, a sufficiently large split was obtained, and a possible enantiomeric purity of the complexes can therefore be measured by direct integration of the separated signals (Table 1). Chemical shifts for each enantiomer were assigned using COSY experiments and revealed upfield or downfield shifts induced by the phosphate reagent (Δδ, spectra c, Figures 3 and 4).

Upon decreasing solvent polarity (lower % acetone), a better nonequivalence between the enantiomeric signals was observed (Figures 3 and 4, spectra b and c). This is interpreted as the result of a closer interactions between the ions. We also note that the spectra in 20% acetone-d_6/C_6D_6 of isolated [**4**][Δ-**1**] and of the mixture of [**4**][BF_4] and [n-Bu_4N][Δ-**1**] (5.7−11.7 equiv) are virtually identical in the aromatic region. This

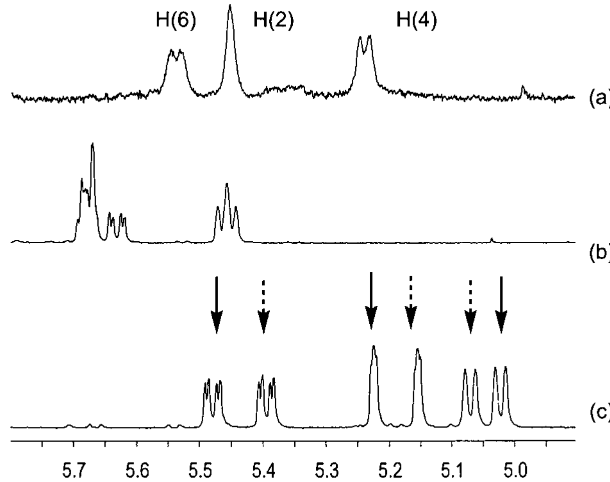

Figure 4. ^{1}H NMR spectra (parts, 400 MHz) of (a) [**5**][PF_6] in 20% acetone-d_6/C_6D_6 and of [**5**][Δ-**1**] in (b) 20% acetone-d_6/C_6D_6 and (c) 5% acetone-d_6/C_6D_6, respectively. The poor quality of spectrum (a) is due to the very low solubility of salt [**5**][PF_6].

Table 1. Differences of Chemical Shift (Δδ, ^{1}H NMR, 400 MHz, 5% Acetone-d_6/C_6D_6) Observed for Protons H(2−6) of Salts [2−5][Δ-1]

	Δδ				
complex	H(2)	H(3)	H(4)	H(5)	H(6)
2		0.029	0.085	0.039	0.111
3		0.095	*a*	0.107	*a*
4		0.154	0.051	0.023	0.078
5	0.070		0.085	0.048	0.049

[a] Not determined due to overlaps between signals.

demonstrates that a rapid exchange of the counterions takes place in solution and that, in the mixture of salts, the $Mn(CO)_3$ complex **4** is essentially associated with the chiral anion **1**.

Finally, we also observe that this method can be applied with equivalent success on chiral $Mn(CO)_3$ complexes with *ortho* (**2**−**4**) or *meta* substituents (**5**, Figure 4).

In conclusion, we have shown that determination of the enantiomeric purity of chiral arene $Mn(CO)_3$ substituted toluene complexes can be realized using TRISPHAT anion **1** as NMR chiral shift reagent. However, this requires—due to the low solubility of the BF_4 or PF_6 salts of the $Mn(CO)_3$ complexes—the preparation and isolation of the [chiral cation][TRISPHAT] salts prior to the analysis. As a purification step is involved, care should therefore be taken to use this methodology on crude materials rather than on already purified compounds.

Experimental Section

Preparation of Arene $Mn(CO)_3$ Complexes 2, 3, and 5. These arene $Mn(CO)_3$ complexes were prepared by the previously described procedures.[12]

Preparation of (η^6-2-trimethylsilyltoluene)$Mn(CO)_3$ (4). $AgBF_4$ (967 mg, 4.97 mmol) and $BrMn(CO)_5$ (1,367 g, 4.97 mmol) were heated for 3 h at reflux in CH_2Cl_2 (20 mL). Then, 2-trimethylsilyltoluene (1.711 g, 10,43 mmol; prepared from the reaction of TMSCl and the Grignard of 2-Br-toluene) was added, and the reaction mixture heated at reflux for 18 h. Treatment under previously reported conditions[12] yielded complex **4** as a yellow powder (1.068 g, 2.74 mmol): yield 55%.

(16) For the anion exchange, e.g., [R_3NH][**1**] + [**2**−**4**][BF_4] to give [R_3NH][BF_4] + [**2**−**4**][**1**], the preferred source of TRISPHAT anion is [cinchonidinium][Δ-**1**], as this salt and the resulting byproduct [cinchonidinium][BF_4] are completely retained on SiO_2 or Al_2O_3 using CH_2Cl_2 as eluent.

(17) With such a diamagnetic chiral shift reagent, heights of peaks can be also considered in making enantiomeric excess determination. See: Pirkle, W. H.; Hoover, D. J. *Top. Stereochem*. **1892**, *13*, 263.

Anal. Calcd for $MnC_{13}H_{16}BO_3F_4Si$: C, 40.03; H, 4.13. Found: C, 39.81; H, 4.14. ^{1}H NMR (200 MHz, acetone-d_6): δ 7.17 (t, J = 6.0 Hz, 1H, H(4)), 7.02 (d, J = 6.5 Hz, 1H, H(6)), 6.6−6.4 (m, 2H, H(3) and H(5)), 2.71 (s, 3H, Me), 0.59 (s, 9H, $SiMe_3$). ^{13}C NMR (50.33 MHz, acetone-d_6): δ 206.27 (brs, CO), 127.67 (s, C-1), 110.25 (s), 108.71 (s, C-2), 106.52 (s), 99.96 (s), 96.15 (s), 21.96 (s, Me), −0.65 (s, $SiMe_3$).

Typical Procedure for the Preparation of the TRISPHAT Salts of the $Mn(CO)_3$ Arene Complexes 2−5. In a 10 mL round-bottomed flask equipped with a magnetic stirring bar, a solution of BF_4 or PF_6 salt of cationic $Mn(CO)_3$ complexes **2**−**5** (1.0 equiv, ∼50 μmol) in acetone (1.0 mL) was added to a limpid solution of [cinchonidinium][Δ-**1**] (1.2 equiv, ∼60 μmol) in acetone (1.0 mL). The resulting mixture was stirred for 10 min and the head of a spatula of basic Al_2O_3 then added prior to concentration in vacuo (water pump then high vacuum). The adsorbed material was then put at the top of a basic Al_2O_3 column (1.0 × 0.5 cm). Elution with CH_2Cl_2 (4−7 mL) afforded the resulting [**2**−**5**][Δ-**1**] in modest to decent yields (26−63%).

Salt [η^6-(1-Methoxy-2-methylbenzene)$Mn(CO)_3$][Δ-TRISPHAT)] or [2][Δ-1]. Preparation followed the general procedure using 18.1 mg of [**2**][BF_4] (49.0 μmol) and 64.8 mg of [cinchonidinium][Δ-**1**] (60.9 μmol) to afford [**2**][Δ-**1**] as a yellow oil (21.8 mg, 43%): R_f 0.26 (Al_2O_3, CH_2Cl_2). ^{1}H NMR (5% acetone-d_6/C_6D_6, 400 MHz): δ 6.35 and 6.31 (t, J = 6.5 Hz, 1H, H(5)); 5.98 and 5.95 (d, J = 6.0 Hz, 1H, H(3)); 5.69 and 5.58 (d, J = 7.0 Hz, 1H, H(6)); 5.51 and 5.43 (t, J = 6.5 Hz, 1H, H(4)); 3.36 and 3.24 (s, 3H, $-OCH_3$); 1.71 and 1.68 (s, 3H, $-CH_3$). ^{31}P NMR (20% acetone-d_6/C_6D_6, 162 MHz): δ −78.92. ES-MS: (+) 260.9 (100%); (−) 768.7 (100%).

Salt [η^6-(1-Chloro-2-methoxybenzene)$Mn(CO)_3$][Δ-TRISPHAT] or [3][Δ-1]. Preparation followed the general procedure using 15.8 mg of [**3**][BF_4] (45.4 μmol) and 59.3 mg of [cinchonidinium][Δ-**1**] (55.7 μmol) to afford [**3**][Δ-**1**] as a pale yellow solid (29.4 mg, 63%): R_f 0.88 (Al_2O_3, CH_2Cl_2). ^{1}H NMR (5% acetone-d_6/C_6D_6, 400 MHz): δ 6.71−6.46 (m, 2H, H(6) + H(4)); 6.16 and 6.06 (d, J = 7.0 Hz, 1H, H(3)); 5.93 and 5.82 (t, J = 6.0 Hz, 1H, H(5)); 3.62 and 3.51 (s, 3H, $-OCH_3$). ^{31}P NMR (20% acetone-d_6/C_6D_6, 162 MHz): δ −73.23. ES-MS: (+) 281.0 (100%); (−) 768.7 (100%).

Salt [η^6-(1-Trimethylsilyl-2-methylbenzene)$Mn(CO)_3$]-[Δ-TRISPHAT] or [4][Δ-1]. Preparation followed the general procedure using 20.4 mg of [**4**][BF_4] (52.3 μmol) and 67.8 mg of [cinchonidinium][Δ-**1**] (63.7 μmol) to afford [**4**][Δ-**1**] as a pale yellow solid (25.8 mg, 49%): R_f 0.80 (Al_2O_3, CH_2Cl_2). ^{1}H NMR (5% acetone-d_6/C_6D_6, 400 MHz): δ 6.82 and 6.72 (dt, J = 6.5, 1.0 Hz, 1H, H(4)); 6.23 and 6.16 (dd, J = 6.5, 1.0 Hz, 1H, H(6)); 5.99 and 5.97 (dt, J = 6.5, 0.5 Hz, 1H, H(5)); 5.89 and 5.74 (d, J = 6.5 Hz, 1H, H(3)); 2.00 and 1.92 (s, 3H, $-CH_3$); 0.09 and 0.06 (s, 9 H, $-Si(CH_3)_3$). ^{31}P NMR (20% acetone-d_6/C_6D_6, 162 MHz): δ −79.61. ES-MS: (+) 302.9 (88%); (−) 767.8 (100%).

Salt [η^6-(1-Methoxy-3-methylbenzene)$Mn(CO)_3$][Δ-TRISPHAT] or [5][Δ-1]. Preparation followed the general procedure using 19.4 mg of [**5**][PF_6] (47.9 μmol) and 61.8 mg of [cinchonidinium][Δ-**1**] (58.0 μmol) to afford [**5**][Δ-**1**] as a yellow oil (12.6 mg, 26%): R_f 0.74 (Al_2O_3, CH_2Cl_2). ^{1}H NMR (5% acetone-d_6/C_6D_6, 400 MHz): δ 6.44 and 6.39 (t, J = 7.0 Hz, 1 H, H(5)); 5.48 and 5.39 (dd, J = 7.0, 2.5 Hz, 1H, H(6)); 5.22 and 5.15 (t br, J = 1.5 Hz, 1H, H(2)); 5.07 and 5.02 (d, J = 6.5 Hz, 1H, H(4)); 3.38 and 3.35 (s, 3H, $-OCH_3$); 1.86 and 1.78 (s, 3H, $-CH_3$). ^{31}P NMR (20% acetone-d_6/C_6D_6, 162 MHz): δ −79.62. ES-MS: (+) 260.9 (92%); (−) 768.7 (100%).

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