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Syntheses of tris(pyrazolyl)methane ligands and {[tris(pyrazolyl)methane]$Mn(CO)_3$}SO_3CF_3 complexes: comparison of ligand donor properties

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Dedicated to Professor Martin A. Bennett on the occasion of his 65th birthday.

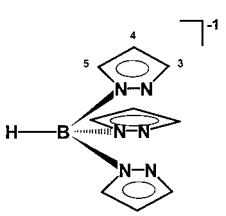
Abstract

The known ligands $HC(pz)_3$, $HC(3,5\text{-}Me_2pz)_3$, $HC(3\text{-}Phpz)_3$, and $HC(3\text{-}^tBupz)_3$ and the new ligand $HC(3\text{-}^iPrpz)_3$ (pz = pyrazolyl ring) are prepared in $CHCl_3$–H_2O using the appropriate pyrazole, an excess of Na_2CO_3, and tetra-*n*-butylammonium bromide as the phase transfer catalyst. Using these conditions, good yields of the ligands are consistently obtained. The new ligand $PhC(pz)_2py$ (py = pyridyl ring) is prepared in the $CoCl_2$ catalyzed condensation reaction of $(pz)_2S{=}O$ and $Ph(py)C{=}O$. The reaction of $HC(pz)_3$, KO^tBu and *para*-formaldehyde followed by quenching with water yields $HOCH_2C(pz)_3$. All of these ligands, except $HC(3\text{-}^tBupz)_3$, react with $[Mn(CO)_5]SO_3CF_3$, prepared in situ from $Mn(CO)_5Br$ and $Ag(SO_3CF_3)$, to yield the respective $[(ligand)Mn(CO)_3]SO_3CF_3$ complex. The carbonyl stretching frequencies and ^{13}C-NMR trends of these complexes indicate that the donor abilities of all of the ligands are fairly similar. The solid state structure of $\{[HC(3\text{-}^iPrpz)_3]Mn(CO)_3\}^+$ shows the $HC(3\text{-}^iPrpz)_3$ ligand is tridentate with the iso-propyl groups rotated away from the $Mn(CO)_3$ core of the cation relieving any possible steric congestion.

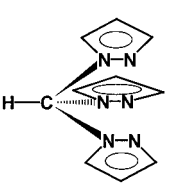
Keywords: Tris(pyrazolyl)methane ligands; Manganese carbonyl complexes; Second generation ligands

1. Introduction

Metal complexes of the tris(pyrazolyl)borate ligand system, first prepared in the late 60's by Trofimenko, are one of the most extensively studied classes of coordination compounds in inorganic chemistry [1]. An important impetus in this chemistry was the introduction, again by Trofimenko, of 'second generation' ligands in which the pyrazolyl rings contain bulky substituents, especially at the three-position [2].



Tris(1-pyrazolyl)borate



Tris(1-pyrazolyl)methane

The isoelectronic tris(pyrazolyl)methane ligands have received less attention [3]. These neutral ligands are formally derived from tris(pyrazolyl)borate ligands by replacing the central boron anion with a carbon atom. Trofimenko reported the syntheses of several tris(pyrazolyl)methane ligands and demonstrated that these neutral ligands bind both early (Cr, Mo, W and Mn) and late transition metals (Co, Ni, and Pd) [4]. Later, Elguero et al. developed an improved procedure for the

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syntheses of these ligands [5]. Despite these early reports, syntheses of 'second generation' tris(pyrazolyl)methane ligands with bulky substituents at the three-position have only recently been reported [6]. One reason for the diminished activity in this area is that the syntheses of the tris(pyrazolyl)methane ligands, with the exception of $HC(pz)_3$ (pz = pyrazolyl ring), are more difficult than the tris(pyrazolyl)borate analogs. In general, yields are only 25–45% and the isolation procedures require several steps, generally including a chromatography. Even the $HC(3,5\text{-}Me_2pz)_3$ ligand was not extensively used until recently, with Enemark publishing the first solid-state structures of complexes containing this ligand in 1995 [3r].

As part of our program to synthesize metal complexes of tris(pyrazolyl)methane and related ligands [6a,b, 7], we have carefully investigated the preparative procedures of the ligands. Reported here are improved preparations of $HC(pz)_3$, $HC(3,5\text{-}Me_2pz)_3$, $HC(3\text{-}Phpz)_3$ and $HC(3\text{-}^tBupz)_3$, and the first report of the syntheses of $HC(3\text{-}^iPrpz)_3$, $PhC(pz)_2py$ (py = pyridyl ring) and $HOCH_2C(pz)_3$. We are also interested in how substitution on the pyrazolyl rings influences the donor properties of the ligands. To that end, we have prepared the $[(ligand)Mn(CO)_3]SO_3CF_3$ complex of each (except with $HC(3\text{-}^tBupz)_3$) and report ligand donor trends based on the carbonyl stretching frequencies and positions of the ^{13}C-NMR resonances.

2. Experimental

2.1. General

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 dry box unless otherwise noted. All solvents were dried and distilled prior to use according to standard methods. ^1H- and ^{13}C-NMR chemical shifts are reported in ppm versus TMS. All reagents were purchased from Aldrich. The pyrazoles not purchased were synthesized according to published procedures; 3-PhpzH [8], 3-^{t}BupzH [8], and 3-^{i}PrpzH [9].

2.2. Tris(1-pyrazoyl)methane (*1*)

Distilled water (294 ml) was added to a 500 ml round bottom flask containing a mixture of pyrazole (20.0 g, 294 mmol) and tetra-*n*-butylammonium bromide (4.7 g, 14.7 mmol). With vigorous stirring, sodium carbonate (187 g, 1.8 mol) was added gradually to the reaction mixture; constant stirring increases the efficiency of the reaction[1]. After cooling to near room temperature (r.t.), chloroform (147 ml) was added and the flask was equipped with a reflux condenser. This mixture was heated at gentle reflux for 3 days over which time it became a pale yellow emulsion. The mixture was allowed to cool to r.t. and filtered through a Büchner funnel to remove the excess base. To the filtrate was added diethyl ether (500 ml) and H_2O (300 ml). The organic layer was separated and the aqueous layer extracted with diethyl ether (3 × 200 ml). The combined organic layers were then washed with saturated brine solution (200 ml). The organic layer was treated with decolorizing charcoal and dried over sodium sulfate. The mixture was filtered and the solvent removed by rotary evaporation. The resulting pale yellow solid (12.6 g, 63%) was then dried under vacuum. M.p. 100–102°C, ([6c] 102–104°C). ^1H-NMR (acetone-d_6): δ 8.73 (s, 1H, *H*C), 7.86 (d, 3H, $J_{HH} = 2.6$, 3-H (pz)), 7.62 (d, 3H, $J_{HH} = 1.7$, 5-H (pz)), 6.40 (d of d, 3-H, $J_{HH} = 1.7$, 2.6, 4-H (pz)).

[1] Caution: this addition is exothermic.

2.3. Tris(3,5-dimethyl-1-pyrazoyl)methane (*2*)

Distilled water (700 ml) was added to a 2 l flask containing a mixture of 3,5-dimethyl pyrazole (68.1 g, 707 mmol) and tetra-*n*-butylammonium bromide (11.4 g, 35 mmol). With vigorous stirring, sodium carbonate (586 g, 4.2 mol) was added gradually to the reaction mixture[1]. After cooling to near r.t., chloroform (350 ml) was added and the flask was equipped with a reflux condenser. This mixture was heated at gentle reflux for 3 days over which time it became an orange–red emulsion. The mixture was allowed to cool to r.t., filtered through a Büchner funnel to remove the excess base, and the organic layer separated from the aqueous layer. The organic layer was washed with distilled water (3 × 50 ml) and dried over sodium sulfate. The drying agent was removed by filtration and the solvent was removed by rotary evaporation. Unreacted pyrazole was removed from the resulting brown solid by sublimation (80°C in oil bath at 0.2 mmHg). The remaining solid was then dissolved in methylene chloride (50 ml) and flushed through a plug of silica with methylene chloride (2 × 250 ml). The solvent was removed by rotary evaporation to afford a yellow–white solid (19.8 g, 65%). M.p. 154–155°C, ([4] 153–154°C). ^1H-NMR (acetone-d_6): δ 8.20 (s, 1H, *H*C), 5.92 (s, 3H, 4-H (pz)), 2.09, 2.03 (s, s, 9H, 9H, 3,5-Me).

2.4. Tris(3-phenylpyrazoyl)methane (*3*)

Distilled water (40 ml) was added to a 100 ml flask containing a mixture of 3-phenylpyrazole (2.88 g, 0.020 mol) and tetra-*n*-butylammonium bromide (0.32 g, 0.99 mmol). With vigorous stirring, sodium carbonate (12.7 g, 120 mmol) was added gradually to the reaction mixture[1]. After cooling to near r.t., chloroform (10 ml) was added and the flask was equipped with a reflux

condenser. This mixture was heated at gentle reflux for 3 days over which time it became a dark yellow emulsion. The mixture was allowed to cool to r.t. and the organic layer separated from the aqueous layer. The aqueous layer was extracted with diethyl ether (1×15 ml). The combined organic layers were washed with distilled water (2×10 ml) and dried over sodium sulfate. The solution was filtered and the solvent was removed by rotary evaporation. The resulting off-white solid was then dissolved in toluene (50 ml) and added to a 100 ml flask containing a catalytic amount of pre-dried *p*-toluenesulfonic acid (0.050 g, 0.27 mmol). The golden solution was heated at reflux for 1 day. After it had cooled to r.t., the solution was neutralized with a 5% aqueous Na_2CO_3 solution (50 ml) and washed with distilled water (3×15 ml). The dark yellow solution was dried over sodium sulfate. The drying agent was removed by filtration and the solvent was removed by rotary evaporation resulting in a dark yellow solid. The solid was dissolved in methylene chloride (20 ml) and chromatographed on a silica gel column (23×4 cm) that was packed and flushed with a 1:1 methylene chloride–toluene solution. When monitored by UV light, the product has a $R_f = 0.3$, while the starting material, 3-PhpzH, has a $R_f = 0.1$. The fractions that contained the desired product were combined and the solvent was removed by rotary evaporation to yield an off-white solid (1.98 g, 67%). M.p. 174–175°C, ([6d] 177–178°C). ^{1}H-NMR (acetone-d_6): δ 8.86 (s, 1H, *H*C), 8.10 (d, 3H, 5-H (pz)), 7.90 (d, 6H, $J_{HH} = 2.6$ Hz, *o*-H (Ph)), 7.42 (dd, 6H, *m*-H (Ph)), 7.35 (d, 3H, *p*-H (Ph)), 6.90 (d, 3, $J_{HH} = 2.6$ Hz, 4-H (pz)).

2.5. Tris(3-i-propylpyrazoyl)methane (**4**)

Distilled water (125 ml) was added to a 250 ml flask containing a mixture of 3-*i*-propylpyrazole (14.1 g, 0.13 mol) and tetra-*n*-butylammonium bromide (2.42 g, 8.0 mmol). With vigorous stirring, sodium carbonate (63.6 g, 0.60 mol) was added gradually to the reaction mixture[1]. After cooling the mixture to near r.t., chloroform (75 ml) was added and the flask was equipped with a reflux condenser. This mixture was heated at gentle reflux for 3 days over which time it became a dark red–orange emulsion. The mixture was allowed to cool to r.t., filtered through a Büchner funnel to remove the excess base, and the organic layer separated from the aqueous layer. The organic fraction was washed with brine (3×30 ml) and dried over sodium sulfate. The drying agent was removed by filtration and the solvent was removed by rotary evaporation. The resulting red oil was dissolved in toluene (100 ml) and added to a 250 ml flask containing a catalytic amount of predried *p*-toluenesulfonic acid (0.086 g, 0.47 mmol). The red solution was heated at reflux for 1 day. After it had cooled to r.t., the toluene solution was neutralized with a 5% aqueous Na_2CO_3 solution (100 ml) and washed with distilled water (3×100 ml). The organic layer was then dried over sodium sulfate, the drying agent removed by filtration and the solvent removed by rotary evaporation resulting in brown oil. An impurity of 3-*i*-propylpyrazole was removed by vacuum distillation at 170°C. The remaining brown oil was dissolved in a 1:1 solution of hexane–toluene (20 ml) and flushed through a plug of silica with 1:1 hexane–toluene (350 ml). The solvent was removed by rotary evaporation to afford a yellow oil (5.04 g, 35%). The oil contains a 5:1 mixture of the desired isomer and an isomer with two pyrazole rings having the iso-propyl group at the three-position and the other one with the iso-propyl group at the five-position. ^{1}H-NMR (acetone-d_6): δ 8.39 (s, 1H, *H*C), δ 7.65 (d, 3H, $J_{HH} = 2.5$ Hz, 5-H (pz)), 6.22 (dd, 3H, 4-H (pz)), 2.96 (septet, 3H, C*H*$(CH_3)_2$), 1.21 (d, 18H, $J_{HH} = 7.0$, CH(C*H*$_3)_2$). ^{13}C-NMR (acetone-d_6): δ 161.1 (5-C (pz)), 129.5 (3C (pz)), 103.8 (4C (pz)), 83.2 (*H*C), 27.8 (C*H*$(CH_3)_2$), 22.6 (CH(C*H*$_3)_2$). FAB$^+$ MS: m/z Anal. Calc. 340.2375, Found: 340.2369 [M]$^+$.

2.6. Tris(3-t-butylpyrazoyl)methane (**5**)

Distilled water (20 ml) was added to a 100 ml flask containing a mixture of 3-*t*-butylpyrazole (2.48 g, 0.020 mol) and tetra-*n*-butylammonium bromide (0.32 g, 1.0 mmol). With vigorous stirring, sodium carbonate (12.7 g, 0.12 mol) was added gradually to the reaction mixture[1]. After cooling the mixture to near r.t., chloroform (10 ml) was added and the flask was equipped with a reflux condenser. This mixture was heated at gentle reflux for 3 days over which time it became a dark yellow emulsion. The mixture was allowed to cool to r.t., filtered through a Büchner funnel to remove the excess base, and the organic layer separated from the aqueous layer. The aqueous layer was then extracted with diethyl ether (3×15 ml). The combined organic fractions were washed with distilled water (2×10 ml) and dried over sodium sulfate. The drying agent was removed by filtration and the solvent was removed by rotary evaporation. The resulting yellow oil was dissolved in toluene (50 ml) and added to a 100 ml flask containing a catalytic amount of pre-dried *p*-toluenesulfonic acid (0.050 g, 0.27 mmol). The golden solution was heated at reflux for 1 day. The solution was cooled to r.t. and neutralized with a 5% aqueous Na_2CO_3 solution (50 ml) and washed with distilled water (3×15 ml). The organic layer was then dried over sodium sulfate, the drying agent removed by filtration and the solvent removed by rotary evaporation resulting in a dark, yellow oil. The oil was dissolved in a 1:1 solution of hexane–toluene (15 ml) and chromatographed on a silica gel column (15×4 cm) that was packed and flushed with a 1:1 hexane–toluene solution. Due to the poor UV visibility of the product, a small aliquot from

each fraction was evaporated and checked by NMR. The fractions that contained the desired product were combined and the solvent volume was again reduced by rotary evaporation giving yellow oil (1.11 g, 43.7%). Most of the oil crystallized neat after several days. The remaining oil was decanted from the crystals by tipping the flask, the crystals washed with cold pentane, the pentane and remaining oil removed to a second flask and crystallized in a low temperature freezer to yield a yellow solid. ^{1}H-NMR (acetone-d_6): δ 8.38 (s, 1H, *H*C), 7.63 (d, 3H, $J_{HH} = 2.5$ Hz, 5H (pz)), 6.28 (d, 3H, $J_{HH} = 2.5$ Hz, 4-H (pz)) 1.26 (s, 27H, C(C*H*$_3$)$_3$).

2.7. Tris-2,2,2-(1-pyrazoyl)ethanol (6)

In a 250 ml Schlenk flask, tris(1-pyrazoyl)methane (1.5 g, 7.0 mmol), potassium *tert*-butoxide (2.0 g, 18 mmol) and *para*-formaldehyde (0.53 g, 18 mmol) were dissolved in THF (100 ml) and stirred at r.t. overnight. Water (100 ml) was added and the mixture was extracted with diethyl ether (3×50 ml). The organic extracts were combined and dried over sodium sulfate and filtered. The solvent was removed in vacuo resulting in a pale yellow solid (1.3 g, 76%). M.p. 113–115°C. ^{1}H-NMR (acetone-d_6): δ 7.65 (d, 3H, $J_{HH} = 1.3$ Hz, 5-H (pz)), 7.30 (d, 3H, $J_{HH} = 2.6$ Hz, 3-H (pz)), 6.39 (dd, 3H, $J_{HH} = 2.2$, 2.2 Hz, 4-H (pz)), 5.04–5.09 (s, 2H, C*H*$_2$). ^{13}C-NMR (acetone-d_6): δ 140.8 (3-C (pz)), 130.3 (5-C (pz)), 106.1 (4-C (pz)), 89.6 (H*C*), 66.8 (*C*H$_2$).

2.8. α,α,α-Bis(1-pyrazoyl)(2-pyridyl)toluene (7)

In a 500 ml Schlenk flask, NaH (4.8 g, 0.20 mol) was mixed in dry THF (200 ml) and stirred at 0°C. Pyrazole (13.6 g, 0.20 mol) were added gradually to the mixture over 15 min and the stirring was continued for 30 min at 0°C resulting in a pale yellow solution. Thionyl chloride (7.3 ml, 0.10 mol) was added drop-wise to this mixture via syringe at 0°C. After stirring for an additional 45 min, benzoyl pyridine (9.2 g, 50 mmol) and a catalytic amount of cobalt (II) chloride (2.5 mmol, 5 mol%) were added and the reaction mixture was heated at reflux overnight. The reaction mixture was allowed to cool to r.t. and then diethyl ether (100 ml) and water (200 ml) were added. The bi-phase solution was then stirred for 30–45 min to quench the cobalt catalyst. The layers were separated and the aqueous phase extracted with diethyl ether (2×100 ml). The combined organic layers were washed with distilled water (50 ml), dried over sodium sulfate and filtered. The solvent was then removed in vacuo and the resulting solid was re-dissolved in methylene chloride and flushed through a plug of silica gel with methylene chloride (2×150 ml). A yellow–brown solid resulted (14.0 g, 93%). M.p. 123–125°C. ^{1}H-NMR (acetone-d_6): δ 8.61 (d, 1H, $J_{HH} = 2.3$ Hz, 6-H (py)), 7.80 (dd, 1H, $J_{HH} = 6.1$, 6.1 Hz, 4-H (py)), 7.58 (d, 3H, $J_{HH} = 1.2$ Hz, 5-H (pz)), 7.44 (d, 3H, $J_{HH} = 2.7$ Hz, 3-H (pz)), 7.33–7.38 (m, 4H, 5-H (py), *p*-H (Ph), *o*-H (Ph)), 7.15–7.16 (m, 3H, *m*-H (Ph), 3-H (py)), 6.33 (dd, 3-H, $J_{HH} = 2.4$, 1.7 Hz, 4-H (pz)). ^{13}C-NMR (acetone-d_6): δ 158.5 (2-C (py)), 148.0 (6-C (py)), 140.1 (*C*C(pz)$_2$(py), 139.6 (5-C (pz)), 136.4 (4-C (py)), 132.0 (3C (pz)), 129.3 (*m*-C (Ph)), 128.5 (*p*-C (Ph)), 127.3 (*o*-C (Ph)), 124.4 (3C (py)), 123.4 (5C (py)), 105.2 (4-C (pz)), 87.0 (Ph*C*(pz)$_2$(py)). These assignments were confirmed by standard Varian gradient enhanced HMQC and HMBC pulse sequences.

2.9. Tris(1-pyrazoyl)methanetricarbonylmanganese triflate (8)

In a 100 ml Schlenk flask wrapped in foil, $Mn(CO)_5Br$ (0.10 g, 0.36 mmol) and $AgSO_3CF_3$ (0.093 g, 0.36 mmol) were combined under a nitrogen atmosphere. These reagents were diluted with 30 ml of dry acetone and stirred at reflux for 45 min. The yellow solution was filtered using a cannula to remove the precipitated AgBr and added to a 100 ml Schlenk flask containing HC(pz)$_3$ (0.077 g, 0.36 mmol). This mixture was then heated at reflux for 1 h and then cooled and stirred an additional 15 h at r.t. The solvent was then removed in vacuo to yield a pale yellow solid. This solid was washed with 10 ml of dry diethyl ether and then filtered to yield a light yellow solid (0.18 g, 85%). M.p. 221–223°C. ^{1}H-NMR (acetone-d_6): δ 9.85 (s, 1H, *H*C), 8.62 (d, 6H, 5-H, 3-H (pz)), 6.75 (s, 3H, 4-H (pz)). ^{13}C-NMR (acetone-d_6): δ 220.5 (*C*O), 148.8 (3-C (pz)), 129.2 (5C (pz)), 109.5 (4-C (pz)), 59.1 (H*C*). FAB$^+$ MS: *m*/*z* Anal. Calc. 353.0195, Found: 353.0209 [M]$^+$. IR (CH_2Cl_2): 2051 (s), 1956 cm^{-1}(m).

2.10. Tris(3,5-dimethyl-1-pyrazoyl)-methanetricarbonylmanganese triflate (9)

The same procedure was followed as with the parent ligand using HC(3,5-Me$_2$pz)$_3$ (0.11 g, 0.36 mmol) yielding the desired product {[HC(3,5-Me$_2$pz)$_3$]Mn(CO)$_3$}-SO_3CF_3 (0.18 g, 85%). M.p. 357–359°C. ^{1}H-NMR (acetone-d_6): δ 8.15 (s, 1H, *H*C), 6.39 (s, 3H, 4-H (pz)), 2.76, 2.61 (s, s, 9H, 9H, CH_3, CH_3). ^{13}C-NMR (acetone-d_6): δ 221.3 (*C*O), 157.1 (3-C (pz)), 145.3 (5-C (pz)), 109.8 (4-C (pz)), 68.1 (H*C*), 14.7 (3-Me), 11.0 (5-Me). FAB$^+$ MS: *m*/*z* Anal. Calc. 437.1154, Found: 437.1134 [M]$^+$. IR (CH_2Cl_2): 2044 (s), 1949 cm^{-1}(m).

2.11. Tris(3-phenyl-1-pyrazoyl)methanetricarbonyl-manganese triflate (10)

The same procedure was followed as with the parent ligand using HC(3-Phpz)$_3$ (0.16g, 0.36 mmol) yielding the desired product {[HC(3-Phpz)$_3$]Mn(CO)$_3$}SO_3CF_3 (0.19 g, 72%). mp 276–278°C. ^{1}H-NMR (acetone-d_6): δ

9.87 (s, 1H, HC), 8.75 (d, 3H, 5-H (pz)), 7.41–7.57 (m, 15H, C_6H_5), 6.76 (d, 3H, 4-H (pz)). ^{13}C-NMR (acetone-d_6): δ 219.5 (*C*O), 162.4 (3-C (pz)), 136.5 (5-C (pz)), 131.7 (pz-*C* (C_6H_5)), 130.8 (*o*-H (C_6H_5)), 130.7 (*p*-H (C_6H_5)), 129.0 (*m*-H (C_6H_5)), 110.8 (4-C (pz)), 76.1 (H*C*). FAB$^+$ MS: *m*/*z* Anal. Calc. 581.1134, Found: 581.1137 [M]$^+$. IR (CH_2Cl_2): 2048 (s), 1956 cm^{-1} (m).

2.12. Tris(3-isopropyl-1-pyrazoyl)-methanetricarbonylmanganese triflate (**11**)

The same procedure was followed as with the parent ligand using HC(3-^{i}Prpz)$_3$ (0.15 g, 0.44 mmol) yielding the desired product {[HC(3-^{i}Prpz)$_3$]Mn(CO)$_3$}SO_3CF_3 (0.13 g, 75%, based on Mn). M.p. 233–235°C. ^{1}H-NMR (acetone-d_6): δ 9.56 (s, 1H, *H*C), 8.50 (s, 3H, 5H (pz)), 6.72 (s, 3H, 4H (pz)), 2.90–3.00 (m, 3H, C*H*(CH$_3$)$_2$), 1.23 (d, 18H, CH(C*H*$_3$)$_2$). ^{13}C-NMR (acetone-d_6): δ 221.6 (*C*O), 168.4 (3-C (pz)), 136.4 (5-C (pz)), 106.2 (4-C (pz)), 75.3 (H*C*), 29.4 (*C*H(CH$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$). FAB$^+$ MS: *m*/*z* Anal. Calc. 479.1603, Found: 479.1602 [M]$^+$. IR (CH_2Cl_2): 2045 (s), 1949 cm^{-1}(m).

Table 1
Crystal data and structure refinement for {[HC(3-^{i}Prpz)$_3$]Mn(CO)$_3$}SO_3CF_3 (**11**)

Empirical formula	$C_{23}H_{28}F_3MnN_6O_6S$
Formula weight	628.51
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	17.564(3)
b (Å)	17.700(3)
c (Å)	18.439(3)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	5732.4(17)
Z	8
D_{calc} (g cm^{-3})	1.457
Absorption coefficient (mm^{-1})	0.600
F(000)	2592
Crystal size (mm^3)	0.08 × 0.06 × 0.06
Theta range for data collection (°)	1.97–22.00
Index ranges	$-17 \le h \le 18$, $-18 \le k \le 18$, $-17 \le l \le 19$
Reflections collected	14 006
Independent reflections	3448 [$R_{int} = 0.1161$]
Completeness to theta = 22.00°	98.2%
Absorption correction	Empirical from SADABS
Max/min transmission	0.9649, 0.9536
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3448/0/362
Goodness-of-fit on F^2	1.063
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.1039$, $wR_2 = 0.2002$
R indices (all data)	$R_1 = 0.1347$, $wR_2 = 0.2202$
Extinction coefficient	0.0047(6)
Largest difference peak and hole (e Å^{-3})	0.635 and −0.778

2.13. Tris-2,2,2-(1-pyrazoyl)ethanoltricarbonylmanganese triflate (**12**)

The same procedure was followed as with the parent ligand using HOCH$_2$C(pz)$_3$ (0.11 g, 0.36 mmol) yielding the desired product {[HOCH$_2$C(pz)$_3$]Mn(CO)$_3$}SO_3CF_3 (0.11 g, 78%). M.p. 214–216°C. ^{1}H-NMR (acetone-d_6): δ 8.74 (d, 3H, 3-H (pz)), 8.61 (s, 3H, 5-H (pz)), 6.75 (dd, 3H, 4-H (pz)) 5.93 (s, 2H, CH_2). ^{13}C-NMR (acetone-d_6): δ 220.2 (*C*O), 148.4 (3-C (pz)), 136.4 (5-C (pz)), 109.2 (4-C (pz)), 84.5 (*C*(pz)$_3$) 60.7 (*C*H$_2$). FAB$^+$ MS: *m*/*z* Anal. Calc. 383.0296, Found: 383.0300 [M]$^+$. IR (CH_2Cl_2): 2051 (s), 1958 cm^{-1}(m).

2.14. α,α,α-Bis(1-pyrazoyl)(2-pyridyl)-toluenetricarbonylmanganese triflate (**13**)

The same procedure was followed as with the parent ligand using PhC(pz)$_2$py (0.11 g, 0.36 mmol) yielding the desired product {[PhC(pz)$_2$py]Mn(CO)$_3$}SO_3CF_3 (0.17 g, 80%). M.p. 207–209°C. ^{1}H-NMR (acetone-d_6): δ 9.49 (d, 1H, 6-H (py)), 8.73 (d, 2H, 3-H (pz)), 8.29 (m, 3H, 5-H (pz), 4-H (py)), 8.08 (dd, 1H, 5-H (py)), 7.817.89 (m, 7H, Ph, 3-H (py), 6.72 (dd, 2H, 4-H (pz)). ^{13}C-NMR (acetone-d_6): δ 221.0 (*C*O), 220.1 (*C*O), 157.3 (6-C (py)), 156.1 (2-C (py)), 149.4 (3-C (pz)), 141.9 (4-C (py)), 137.8 (5-C (pz)), 133.3 (3-C (py)), 132.7 (*m*-C Ph), 130.7 (*o*-C Ph), 129.8 (*C*C(pz)$_2$(py)), 127.9 (5-C (py)), 126.7 (*p*-C Ph), 109.7 (4-C (pz)), 83.6 (Ph*C*(pz)$_2$(py). FAB$^+$ MS: *m*/*z* Anal. Calc. 440.0555, Found: 440.0569 [M]$^+$. IR (CH_2Cl_2): 2049 (s), 1956 cm^{-1}(m).

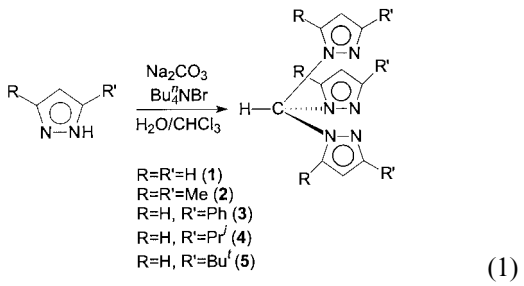
2.15. Crystallographic studies

Crystal, data collection, and refinement parameters are given in Table 1. Compound **11** crystallized in the orthorhombic space group *Pbca*. The structure was solved using direct methods and was completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Empirical absorption corrections were applied. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were refined as isotropic contributions and with thermal parameters set to 1.2 or 1.5 times that of the parent atom. The large thermal parameters for the atoms in the triflate ion suggest the presence of end-for-end disorder about its center. The high *R* value for this structure can be attributed to diffuse diffraction from the sample, and the likelihood of disorder associated with the triflate ion.

3. Results and discussion

3.1. Syntheses of ligands

Although the original preparations of $HC(pz)_3$ and $HC(3,5\text{-}Me_2pz)_3$ were from the direct reaction of the appropriate pyrazolate and $CHCl_3$ [4,12c] and liquid–liquid phase transfer conditions were used in one case [10], most recent preparations use a solid–liquid phase-transfer procedure [5,6c,d]. We have determined that standard $CHCl_3$–H_2O phase transfer conditions coupled with replacing the K_2CO_3, used as the base in the earlier preparations, with a large excess of Na_2CO_3 leads to higher yields and substantially less darkening of the reaction solutions over the 3 days at reflux needed for these reactions to go to completion, Eq. (1).



(1)

Using these conditions, we consistently observe yields over 60% for both $HC(pz)_3$ and $HC(3,5\text{-}Me_2pz)_3$, a major improvement especially for the latter ligand. The modified literature preparation reported a yield of 42% for $HC(3,5\text{-}Me_2pz)_3$ using the solid–liquid phase-transfer procedure [5], but in our hands consistently gave yields of ca. 25%. In addition, because the reaction proceeds with substantially less discoloration, our purification procedure involves washing the product through a plug of silica rather than a full chromatography. Yields ranging from 17 to 42% have been reported using the original Trofimenko preparation that involves a sublimation step to purify the product [3w,4,6e].

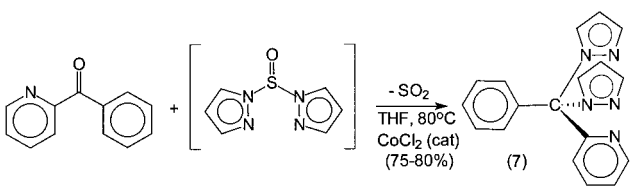
As observed previously in the preparation of $HC(3\text{-}Phpz)_3$ [6c], with this pyrazole reaction 1 yields a number of regioisomers that isomerize to the desired 3-isomer in the presence of anhydrous *p*-toluenesulfonic acid in toluene [6c]. The same result is observed in the synthesis of the new ligand $HC(3\text{-}^iPrpz)_3$, except in this case the isomerization reaction yields a 5:1 mixture of the desired $HC(3\text{-}^iPrpz)_3$ and an isomer with a 2:1 ratio of pyrazolyl-rings, presumably $HC(5\text{-}^iPrpz)(3\text{-}^iPrpz)_2$. As reported previously [6d], $HC(3\text{-}^tBupz)_3$ is hard to crystallize. In the preparation reported here, the oil formed after removal of the solvent from the purified product largely crystallizes over several days.

The methine hydrogen of the $HC(pz)_3$ ligand is acidic and can be removed [3o,14]. Once deprotonated, we have shown that an alcohol functional group may be introduced using *para*-formaldehyde and water, Eq. (2).

$$HC(pz)_3 + KO^tBu \xrightarrow[2)CH_2O\ 3)H_2O]{THF} \underset{(6)}{HOCH_2C(pz)_3} \quad (2)$$

This new ligand allows for an increase in the hydrophilic nature of the system. In other studies, we have modified this ligand to prepare new ligands with solubility properties that allow dissolution either in water or typical organic solvents, depending on the modification [11]. Analogous deprotonation chemistry is successful for the other 3-substituted ligands described here, but not with $HC(3,5\text{-}Me_2pz)_3$ [11].

The syntheses of unsymmetrical ligands related to tris(pyrazolyl)methane ligands, such as $HC(pz)_2py$, has been developed by Canty [12]. The reaction used is a metal catalyzed condensation of $(pz)_2C{=}O$, prepared from the reaction of pyrazolate and phosgene, with aldehydes to yield the desired ligand and CO_2. We have shown that this condensation chemistry is also successful with ketones, but have found that using $(pz)_2S{=}O$, [13] derived from thionyl chloride, provides a more efficient route and avoids the use of phosgene, Eq. (3).

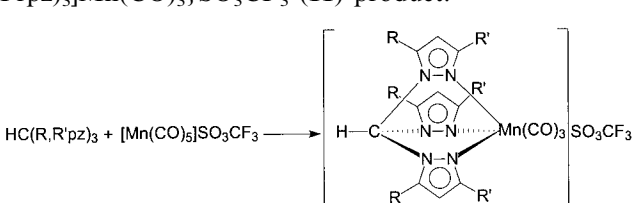


(3)

Unfortunately, similar chemistry using substituted pyrazolyl rings is unsuccessful.

3.2. Syntheses of metal complexes

Reaction of these ligands with $Mn(CO)_5SO_3CF_3$, prepared in situ from $Mn(CO)_5Br$ and $AgSO_3CF_3$, results in the preparation of the respective $[(ligand)Mn(CO)_3]SO_3CF_3$, Eq. (4). The complex $\{[HC(pz)_3]Mn(CO)_3\}PF_6$ has been reported previously [4]. As expected, the reaction was unsuccessful with the bulky 'tetrahedral enforcer' $HC(3\text{-}^tBupz)_3$ ligand. The reaction using the $HC(3\text{-}^iPrpz)_3$–$HC(5\text{-}^iPrpz)(3\text{-}^iPrpz)_2$ ligand mixture was carried out with a slight excess of $HC(3\text{-}^iPrpz)_3$ and yielded only the desired $\{[HC(3\text{-}^iPrpz)_3]Mn(CO)_3\}SO_3CF_3$ (**11**) product.



(4)

The complexes are air stable and soluble in acetone and CH_2Cl_2.

The IR stretching frequencies and the location of the ^{13}C-NMR carbonyl resonances for these complexes are provided in Table 2.

Table 2
IR and ^{13}C-NMR data on [(Ligand)Mn(CO)$_3$]SO$_3$CF$_3$

	Ligand	IR (ν CO) cm^{-1}	^{13}C (CO) ppm
1	HC(pz)$_3$	1956, 2051	220.5
2	HC(3,5-Me$_2$pz)$_3$	1949, 2044	221.3
3	HC(3-Phpz)$_3$	1956, 2048	219.5
4	HC(3-Pr^{i}pz)$_3$	1949, 2045	221.6
5	HOCH$_2$C(pz)$_3$	1958, 2051	220.2
6	PhC(pz)$_2$py	1956, 2049	220.1(2), 221.0(1)

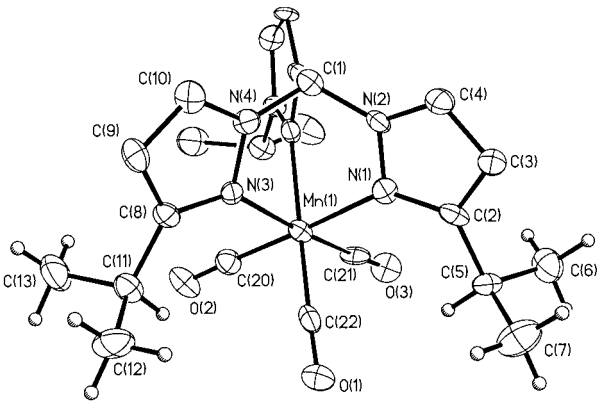


Fig. 1. ORTEP diagram of {[HC(3-^{i}Prpz)$_3$]Mn(CO)$_3$}$^+$.

Table 3
Selected bond distances (Å) and angles (°) for {[HC(3-^{i}Prpz)$_3$]Mn(CO)$_3$}$^+$

Bond distances	
Mn–N(1)	2.054(8)
Mn–N(3)	2.079(8)
Mn–N(5)	2.083(7)
Mn–C(20)	1.808(11)
Mn–C(21)	1.789(11)
Mn–C(22)	1.791(12)
C(1)–N(2)	1.428(12)
C(1)–N(4)	1.433(12)
C(1)–N(6)	1.463(11)
Bond angles	
N(1)–Mn–N(3)	85.3(3)
N(1)–Mn–N(5)	85.8(3)
N(3)–Mn–N(5)	83.9(3)
C(20)–Mn–C(21)	89.0(5)
C(20)–Mn–C(22)	89.8(5)
C(21)–Mn–C(22)	90.1(4)
N(1)–Mn–C(21)	93.2(4)
N(1)–Mn–C(22)	91.1(4)
N(3)–Mn–C(20)	92.5(4)
N(3)–Mn–C(22)	93.0(4)
N(5)–Mn–C(20)	93.2(4)
N(5)–Mn–C(21)	93.0(4)
N(1)–Mn–C(20)	177.7(4)
N(3)–Mn–C(21)	176.6(4)
N(5)–Mn–C(22)	175.7(4)
N(2)–C(1)–N(4)	111.1(8)
N(2)–C(1)–N(6)	110.5(8)
N(4)–C(1)–N(6)	109.6(7)

Given the variation in the substitution on the pyrazolyl rings, the changes in the carbonyl stretching frequencies are surprisingly small. Although the spread is only ca. 7 cm^{-1}, the values fall into two groups, with the alkyl-substituted ligands in one group showing lower values and all the other ligands in the other group. The alkyl-substituted ligands are slightly more basic; the increased electron density at the metal increases the backbonding to the carbonyl ligands. Surprisingly, the PhC(pz)$_2$py ligand, containing the more basic pyridyl ring, falls in the latter group. The variations in the carbonyl ^{13}C-NMR resonances are also small but the values fall into the same two groups. The slightly more basic alkyl-substituted ligands have the higher values, again indicating more backbonding [15]. For {[PhC(pz)$_2$py]Mn(CO)$_3$}SO$_3$CF$_3$, the carbonyl resonance for the CO ligands *trans* to the pz groups fall into the lower group and the resonance for the CO *trans* to the py into the higher group. Both the IR and ^{13}C-NMR trends indicate that the alkyl-substituted ligands donate slightly more electron density to the metal, but the differences are small.

4. X-ray structure of {[HC(3-Pr^{i}pz)$_3$]Mn(CO)$_3$}SO$_3$CF$_3$ (11)

Crystals of {[HC(3-^{i}Prpz)$_3$]Mn(CO)$_3$}SO$_3$CF$_3$ were grown by layering hexane over an acetone solution of the complex. Fig. 1 shows an ORTEP diagram and selected bond distances and angles are collected in Table 3. The manganese is surrounded by three nitrogen atoms from the HC(3-^{i}Prpz)$_3$ ligand and three carbonyl ligands in a nearly octahedral arrangement. The chelate rings of the HC(3-^{i}Prpz)$_3$ ligand restrict the N–Mn–N angles to an average of 85°. The C–Mn–C angles of the carbonyl groups are nearly 90°.

This first structural characterization of this new ligand demonstrates that despite the substitution of the bulky iso-propyl substituents the ligand is tridentate with no distortions caused by steric interaction. The iso-propyl substituents are oriented away from the Mn(CO)$_3$ center of the cation reducing steric strain. This same arrangement is observed in the 6-coordinate structure of [HB(3-^{i}Prpz)$_3$]MoO$_2$(OMe) [16] and related molecules [17], but not in 4-coordinate structures of this ligand such as [HB(3-^{i}Prpz)$_3$]Co(NCS) [9]. The Mn–N bond distances average 2.07 Å, exactly the distance observed in the structure of the neutral tris(pyrazolyl)borate complex [HB(3,5-Me$_2$pz)$_3$]Mn(CO)$_3$ [18], indicating that there is no large steric strain causing elongation of these bonds. Overall, this tris(pyrazolyl)borate structure is very similar to that reported here for **11**, except the B–N distance is longer (average 1.53 Å) than the analogous C–N distance (average 1.44 Å) due to the larger size of boron.

5. Conclusions

The synthetic methodology reported here represents a significant improvement in the preparation of tris(pyrazolyl)methane ligands, especially HC(3,5-$Me_2pz)_3$. The main changes are the use of standard phase transfer reaction conditions and the replacement of K_2CO_3 as the base with a large excess of Na_2CO_3. These methods have been used to prepare the new ligand HC(3-^{i}Prpz)$_3$. We have shown that tris(pyrazolyl)methane ligands without 5-substituents can be derivatized at the methine carbon atom to form the ligand $HOCH_2C(pz)_3$. We have also shown that the metal catalyzed condensation of $(pz)_2C{=}O$ with aldehydes is successful with ketones, but the reaction is more successful using $(pz)_2S{=}O$ in place of $(pz)_2C{=}O$. All of these ligands form [(ligand)$Mn(CO)_3$]SO_3CF_3 complexes, with the exception of HC(3-^{t}Bupz)$_3$. The carbonyl stretching frequencies and locations of the carbonyl resonances in the ^{13}C-NMR spectra indicate a very small variation in the basicity of the various ligands. The structure of $\{[HC(3\text{-}^i Prpz)_3]Mn(CO)_3\}^+$ shows this ligand is tridentate with no unusual steric congestion caused by the iso-propyl substituents.

6. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge crystallographic Centre, CCDC no. 142413 for compound **11**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk, or www: http://www.ccdc.cam.ac.uk).

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