SYNTHESIS AND CARBON-13 NMR SPECTROSCOPY OF POLY(PYRAZOL-1-YL)ALKANE LIGANDS

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Summary — The carbon-13 chemical shifts and ^1H-^{13}C coupling constants of twelve polypodal ligands belonging to bis(pyrazol-1-yl)- and tris(pyrazol-1-yl)-methane classes are described. The chemical shifts show high internal consistency: for instance, a previously-reported additive model predicts, with great accuracy, the chemical shift of the central sp^3 carbon. Coupling constants proved to be useful tools for the assignment of pyrazole carbons. The $^1J(^1H$-$^{13}C)$ coupling of the central carbon is linearly related to the basicity of the pyrazole substituent in tris(pyrazol-1-yl)methanes.

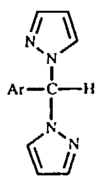
The use of polypyrazolylmethanes as ligands in coordination chemistry is increasing in an ever quicker pace. Save for paramagnetic complexes, carbon-13 NMR spectroscopy is the method of reference to identify the resulting complexes. Thus, a detailed ^{13}C NMR knowledge of the free ligands is necessary. However, the ligands are often found spread over different publications, making comparisons difficult.

For polypyrazolylborates we carried out such a systematic study[1], which proved useful for other workers[2,3]. In the case of polypyrazolylmethanes, a preliminary account was published some years ago[4]. We here present a ^{13}C NMR study of twelve bis- and tris-pyrazolylmethanes, eight of them never previously described. Those already known, bis(pyrazolyl)phenylmethane, **1**, tris(pyrazolyl)methane, **5**, tris(pyrazolyl)ethane, **8**, and tris(3,5-dimethylpyrazolyl)methane, **11**, have been extensively used in coordination chemistry, see table 1.

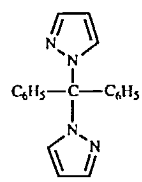
TABLE 1 - COMPLEXES PREPARED WITH POLYPYRAZOLYLMETHANES

Compound	References
1, $(pz)_2PhCH$	5-9
5, $(pz)_3CH$	7,8,10-26
8, $(pz)_3CCH_3$	17,24
11, $(dmpz)_3CH$ (L)	27[a]

([a]) $[Rh(CO)_2L]^+BF_4^-$, $[Ir(CO)_2L]^+BF_4^-$.



1, Ar = C_6H_5
2, Ar = 3-$MeOC_6H_4$
3, Ar = 2-BrC_6H_4



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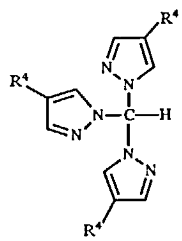
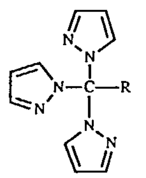
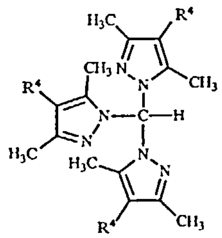


5, R^4 = H
6, R^4 = CH_3
7, R^4 = Br



8, R = CH_3
9, R = C_2H_5
10, R = $CH_2C_6H_5$



11, R^4 = H
12, R^4 = Br

RESULTS

The ^{13}C NMR chemical shifts and ^1H-^{13}C coupling constants (first-order analysis) are collected in table 2.

The chemical shifts of table 2 show no unexpected features. Substitution on the phenyl ring of compound **1** by a methoxy group, **2**, or a bromine atom, **3**, does not affect the pyrazole carbon chemical shifts. The effects of the substituent at position 4 (compounds **5**, **6** and **7**) is similar to those observed for simpler pyrazoles[28]. The substituent on the sp^3 carbon, methyl, **8**, ethyl, **9**, or benzyl, **10**, modify the chemical shifts of this carbon in a classical way[29] and has very little effect on pyrazole carbons, although it

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TABLE 2 - CARBON-13 NMR PARAMETERS OF LIGANDS 1-12 IN DEUTERIOCHLOROFORM

Comp.	C3	C4	C5	C (sp^3)	Substituents
1[a]	140.7 ^1J=186.0 ^2J=6.0, ^3J=8.0	106.5 ^1J=177.5 ^2J=^2J=9.5	129.7 ^1J=188.0 (br)	77.7 ^1J=151.5 ^3J=4.0 (Ho)	136.1 (C1'), 126.9 (C2'), 128.8 (C3'), 129.2 (C4')
2	140.7 ^1J=186.2 ^2J=5.8, ^3J=8.5	106.5 ^1J=177.7 ^2J=8.5 (H5), ^2J=10.4 (H3)	129.6 ^1J=188.4 ^2J=9.0, ^3J=4.7 ^3J=2.9 (CH)	77.6 ^1J=151.8	137.5 (C1') (^2J=8.7, ^3J=5.7), 112.8 (C2')(^1J=156.4), 159.8 (C3'), 114.5 (C4') (^1J=162.2), 129.8 (C5') (^1J=160.7), 119.1 (C6') (^1J=161.7), 55.2 (OMe) (^1J=144.0)
3	140.9 ^1J=186.3 ^2J=5.8, ^3J=8.6	106.4 ^1J=178.0 ^2J=8.4 (H5), ^2J=10.4 (H3)	129.6 ^1J=188.2 ^2J=9.1, ^3J=4.5 ^3J=2.5 (CH)	77.1 ^1J=153.7 ^3J=3.2 (H0)	135.1 (C1'), 123.1 (C2'), 133.2 (C3'), 130.8 (C4') (^1J=154.8, ^3J=8.7), 127.7 (C5') (^1J=152.9, ^3J=7.8), 128.7 (C6') (^1J=161.9)
4	140.3 ^1J=186.1 ^2J=5.8, ^3J=8.7	105.4 ^1J=177.3 ^2J=8.7 (H5), ^2J=10.3 (H3)	132.6 ^1J=187.9 ^2J=9.6, ^3J=4.3	87.6	140.4 (C1'), 128.2 (C2'), 127.9 (C3'), 129.1 (C4')
5[b]	141.7 ^1J=188.4 ^2J=5.8, ^3J=8.7	107.2 ^1J=179.9 ^2J=7.8 (H5), ^2J=10.6 (H3)	129.4 ^1J=191.7 ^2J=9.6, ^3J=4.6 ^3J=2.5 (CH)	83.2 ^1J=167.9	
6	142.3 ^1J=184.1 ^3J=8.8, ^3J=4.4 (Me)	117.5 ^2J=5.9, ^2J=8.4	127.6 ^1J=187.5	83.1 ^1J=166.3	8.8 (Me-4) (^1J=127.5)
7[c]	141.7 ^1J=195.1 ^3J=6.9	94.6 ^2J=5.8 (H5) ^2J=8.4 (H3)	130.5 ^1J=198.5 ^3J=2.3	81.6 ^1J=171.5	
8	141.4 ^1J=187.0 ^2J=5.8, ^3J=8.8	106.8 ^1J=178.3 ^2J=8.4 (H5), ^2J=10.5 (H3)	129.1 ^1J=190.1 ^2J=9.6, ^3J=4.3	90.2 ^2J=5.1 (Me)	26.4 (Me) (^1J=133.0)
9	141.1 ^1J=186.8 ^2J=5.8, ^3J=8.7	106.3 ^1J=178.2 ^2J=8.4 (H5), ^2J=10.4 (H3)	129.8 ^1J=190.4 ^2J=9.6, ^3J=4.3	92.2 ^2J=5.8 (CH_2)	33.8 (CH_2) (^1J=131.3, ^2J=4.4), 8.6 (CH_3) (^1J=127.4, ^2J=4.4),
10	140.8 ^1J=186.9 ^2J=5.7, ^3J=8.6	106.7 ^1J=178.2 ^2J=8.3 (H5), ^2J=10.4 (H3)	130.5 ^1J=190.8 ^2J=9.6, ^3J=4.4	92.4 ^2J=6.6 (CH_2)	44.7 (CH_2) [^1J=132.9, ^3J=3.9 (H_O)] 133.6 (C1') 130.8 (C2'), 128.1 (C3'), 127.4 (C4')
11	148.7 ^2J=^2J=(Me)=6.0	107.6 ^1J=13.0 ^3J=^3J=3.3 (Me)	140.8 ^2J=^2J=(Me)=6.9	80.7 ^1J=163.8	13.8 (Me-3) (^1J=127.2) 10.7 (Me-5) (^1J=129.0)
12	148.1	98.2	139.2	78.8	13.1 (Me-3), 10.7 (Me-5)

([a]) Values from reference 4. ([b]) Chemical shifts already published in reference 4. ([c]) Solvent: DMSO-d_6.

can be noticed that $\delta_{C3} = 196.73 - 0.429\delta_{C5}$, $n = 3$, $r^2 = 1.00$.

In a previous publication[4], we proposed an additive model to discuss the chemical shift of the central carbon of polyazolylmethanes. Compound **4**, $(pz)_2Ph_2C$, was one of the rare combinations of pyrazol-1-yl and phenyl residues which was missing. The model was C(sp^3) = constant term + 2 (Δpyrazol-1-yl) + 2 (Δphenyl) + Δphenyl/phenyl + 4 (Δphenyl/-pyrazol-1-yl) + Δpyrazol-1-yl/pyrazol-1-yl = 2.85 + 2 (35.10) + 2 (21.10) – 3.35 + 4 (–4.06) – 8.01 = 87.65. The signal was actually observed at 87.62 ppm, rounded up to 87.6 in table 2.

The coupling constants of the three pyrazole carbons have standard values[30] very characteristic of the position. Carbon C5 shows a ^3J coupling constant with the C(sp^3)-H. The central sp^3 carbon atom is coupled with the adjacent methyl or methylene protons (^2J ~ 5.8 Hz) (compounds **8, 9, 10**) and with the phenyl *ortho* protons (^3J ~ 3.5 Hz) (compounds **1, 3**) but not with pyrazole C5-H proton (also a ^3J). A comparison of trispyrazolylmethanes **5, 6, 7** and **11**, shows that the C(sp^3) ^1J coupling constant is sensitive to the pyrazole nature, particularly to its basicity[31]: $^1J = 173.08 - 2.20pK_a$, $n = 4$, $r^2 = 0.993$.

EXPERIMENTAL

Melting points were determined on a capillary Büchi 512 apparatus and are uncorrected. Analyses were determined using in-house facilities. The ^{1}H and ^{13}C NMR spectra were taken with a Bruker AC 200 working at 200.135 and 50.324 MHz, respectively. Chemical shifts (δ) are given from internal tetramethylsilane with an accuracy of ±0.01 ppm for ^{1}H NMR and ±0.1 ppm for ^{13}C NMR. Coupling constants (J) were measured with digital resolutions of 0.2 Hz. The following compounds have already been described: **1**[32-34], **5**[35,36], **8**[17,24] and **11**[35]. Mass spectra were recorded on a Hitachi-Perkin-Elmer VG-12-250 spectrometer working at 75 eV (mass-to-charge units are in Thomson, the recently introduced unit to replace the old *m/z* notation[36]).

(3-METHOXYPHENYL)BIS(PYRAZOL-1-YL)METHANE, **2**

2 was prepared by the reaction of bis(pyrazol-1-yl)methanone, pz_2CO, and 3-methoxybenzaldehyde, in the manner described for related bis(pyrazol-1-yl)alkanes[23]. Reaction for **2** (gentle warming), followed by recrystallization from hot hexane/charcoal gave the required compound in 50-60% yield, m.p. 47 °C. *Elem. anal.*, found % (calcd for $C_{14}H_{14}N_4O$): C, 65.8 (66.1); H, 5.7 (5.5); N, 22.2 (22.0). ^{1}H NMR ($CDCl_3$): 7.70 (CH, s), 7.63 (H3, d, J_{34} = 1.6 Hz), 6.33 (H4, dd), 7.52 (H5, d, J_{45} = 2.3), 6.56 (H2', m), 6.61 (H6', m), 7.28 (H5', t, J_o = 8.0), 6.91 (H4', dd, J_o = 8.2, J_m = 2.4), 3.73 (s, OMe); MS, Th (%): 254 (M^+, 39), 188 (27) and 187 (100).

(2-BROMOPHENYL)BIS(PYRAZOL-1-YL)METHANE, **3**

With the same procedure but using 2-bromobenzaldehyde compound **3** was obtained which was recrystallized from the minimum volume of hot hexane, m.p. 73 °C. *Elem. anal.*, found % (calcd for $C_{13}H_{11}N_4Br$): C, 60.2 (60.4); H, 4.0 (4.3); 21.7 (21.7). ^{1}H NMR ($CDCl_3$): 7.96 (CH, s), 7.68 (H3, d, J_{34} = 1.4 Hz), 6.37 (H4, dd), 7.39 (H5, d, J_{45} = 2.3), 7.64 (H3', dd, J_o = 7.8, J_m = 1.9), 7.24-7.35 (H4' and H5', m), 6.84 (H6', dd, J_o = 8.0, J_m = 2.3); MS, Th (%): 304 (M^+, 1), 302 (M+, 1), 237 (16), 235 (17), 224 (14), 223 (83), 157 (14) and 156 (100).

DIPHENYLBIS(PYRAZOL-1-YL)METHANE, **4**

The compound $(pz)_2Ph_2C$ was prepared, in 50% yield, by the reaction of potassium pyrazolide with Ph_2CCl_2 according to the procedure described for related compounds[37]. The compound will be described in full detail elsewhere[38].

TRIS(4-METHYLPYRAZOL-1-YL)METHANE, **6**

In a reaction flask provided with a condenser and a magnetic stirring bar, were placed 24 mmol of 4-methylpyrazole, 120 mmol of anhydrous potassium carbonate, 1.2 mmol of tetrabutylammonium bromide and 25 ml of good-quality chloroform. After 10 h of reflux under vigorous stirring, the hot suspension was filtered off, the solid washed with hot chloroform, and filtrate and washings combined. The organic phase was dried over sodium sulphate, the chloroform was evaporated under reduced pressure, and the residue purified by column chromatography over silica (eluant: 8:2 Et_2O/hexane). Compound **6**, R_f = 0.44, yield: 40%, m.p. 151-3 °C. *Elem. anal.*, found % (calcd for $C_{13}H_{16}N_6$): C, 61.2 (60.9); H, 6.5 (6.3); N, 33.0 (32.8). ^{1}H NMR ($CDCl_3$): 8.16 (CH, s), 7.46 (H3, s), 2.06 (CH_3-4, s), 7.30 (H5, s); (DMSO-d_6): 8.62 (CH, s), 7.44 (H3, s), 2.00 (CH_3-4, s), 7.60 (H5, s); MS, Th (%): 256 (M^+, 20) and 175 (100).

TRIS(4-BROMOPYRAZOL-1-YL)METHANE, **7**

This compound has been prepared in two ways. The first one is similar to the preceding synthesis. In a flask provided with magnetic stirring and a condenser, were placed 24 mmol of 4-bromopyrazole[39], 48 mmol of powdered potassium hydroxide, 1.2 mmol of tetrabutylammnium bromide and 75 ml of good-quality chloroform. After 2 h of reflux and vigorous stirring, the suspension was filtered, the solid washed with hot chloroform and the organic solution evaporated under a vacuum. The residue was purified by column chromatography over silica (eluant: 9:1 hexane/AcOEt), R_f = 0.22, yield, 22%, m.p. 170-1 °C. *Elem. anal.*, found % (calcd for $C_{10}H_7Br_3N_6$): C, 26.3 (26.6); H, 1.7 (1.6); N, 18.4 (18.6). ^{1}H NMR ($CDCl_3$): 8.18 (CH, s), 7.63 (H3, d, J_{35} = 0.6 Hz), 7.66 (H5, d); (DMSO-d_6): 8.95 (CH, s), 7.83 (H3, d, J_{35} = 0.6 Hz), 8.22 (H5, d); MS, Th (%): 450 (M^+, 6) and 305 (100).

Compound **7** can also be obtained by bromination of $(pz)_3CH$, **5**. A mixture of **5** (2.3 mmol), bromine (3.2 mmol) in 25 ml of chloroform was heated under reflux for 2 h. After cooling, the solution was neutralized with sodium carbonate, filtered and evaporated to dryness: 30% yield of **7**.

TRIS(PYRAZOL-1-YL)PROPANE, **9**

Compound **9** was prepared like compound **8**[17] but using ethyl iodide instead of methyl iodide. The method is similar to that used by Katritzky[33] for the C-alkylation of bis(pyrazol-1-yl)methane: m.p. 54-5 °C (hexane), yield: 72%. *Elem. anal.*, found % (calcd for $C_{12}H_{14}N_6$): C, 59.7 (59.5); H, 6.1 (5.8); N, 34.7 (34.7). ^{1}H NMR ($CDCl_3$): 1.14 (CH_3, t, J = 7.3 Hz), 3.36 (CH_2, m), 7.68 (H3, dd, J_{34} = 1.6, J_{35} = 0.8 Hz), 6.32 (H4, dd), 7.08 (H5, dd, J_{45} = 2.9 Hz); MS, Th (%): 242 (M^+, 11), 176 (11), 175 (98) and 107 (100).

PHENYLTRIS(PYRAZOL-1-YL)ETHANE, **10**

Compound **10** was obtained like the preceding compound but using benzyl bromide as alkylating agent: m.p. 62-3 °C (hexane), yield: 60%. *Elem. anal.*, found % (calcd for $C_{17}H_{16}N_6$): C, 66.9 (67.1); H, 5.3 (5.3); N, 27.8 (27.6). ^{1}H NMR ($CDCl_3$): 4.81 (CH_2, s), 7.69 (H3, dd, J_{34} = 1.7, J_{35} = 0.8 Hz), 6.31 (H4, dd), 7.09 (H5, dd, J_{45} = 2.6 Hz), 6.83-7.29 (Ph, m); MS, Th (%): 304 (M^+, 4), 237 (21), 236 (45), 235 (39) and 213 (100).

TRIS(4-BROMO-3,5-DIMETHYLPYRAZOL-1-YL)METHANE, **12**

From 4-bromo-3,5-dimethylpyrazole[39] and chloroform under conditions of phase-transfer catalysis, like compound **7**. Reflux was maintained overnight and purification was carried out by column chromatogrpahy on silica (eluant: 3:7 hexane/ethyl acetate). Compound **12**: m.p. 218-20 °C, yield: 9%. *Elem. anal.*, found % (calcd for $C_{16}H_{19}Br_3N_6$): C, 36.2 (35.9); H, 3.4 (3.6); N, 15.8 (15.7). ^{1}H NMR ($CDCl_3$): 2.20 (CH_3, s), 2.02 (CH_3, s), 8.05 (CH, s); MS, Th (%): 536 (M^+, 5), 450 (7), 307 (34) and 305 (100).

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