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COMMUNICATION

SYNTHESIS, ^{1}H AND ^{13}C NMR CHARACTERIZATION OF METHYL-*MESO*-TETRA(4-PYRIDYL)-PORPHYRINATO THALLIUM(III): Tl(tpyp)CH_3

SUH-SHING TANG, MING-TORNG SHEU, YUN-HUIN LIN, I-CHIH LIU
and JYH-HORUNG CHEN*

Department of Chemistry, National Chung-Hsing University, Taichung 40227, Taiwan

and

SHIN-SHIN WANG

Union Chemical Laboratories, Hsin-Chu 30034, Taiwan

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Abstract—The ^{13}C resonance of the axial methyl group observed at 1.2 ppm (24°C) [with $^{1}J(^{205}Tl—^{13}C)$ = 5752.3 Hz and $^{1}J(^{203}Tl—^{13}C)$ = 5703.3 Hz] in $CDCl_3$ and a doublet with upfield resonance at -56.7 ppm by a solid-state ^{13}C CP/MAS NMR (at carbon frequency 50.33 MHz) measurement provide an evidence that the methyl group was coordinated to the Tl atom of methyl-*meso*-tetra(4-pyridyl)-porphyrinato thallium(III).

Henrick *et al.*[1] first reported the synthesis and X-ray structure of methyl-*meso*-tetraphenyl-porphyrinato thallium(III), Tl(tpp)CH_3. The methyl protons of the apical ligand were observed as a doublet with $^{2}J(Tl—^{1}H) = 724\pm2$ Hz at $\delta = -3.49$ ppm in a $CDCl_3$ solvent. All other ^{13}C signals except the axial methyl carbon in the porphyrin were clearly observed. They claimed that the solubility precluded observation of the ^{13}C resonance owing to the CH_3—Tl. Recently, Sheu *et al.*[2] reported that the ^{13}C resonance of the axial methyl group of Tl(tpp)CH_3 was observed at 0.4 ppm (24°C) [with $^{1}J(Tl—^{13}C)$ coupling constant 5774 Hz] in a $CDCl_3$ solvent. When the phenyl group was substituted by a pyridyl group, it became methyl-*meso*-tetra(4-pyridyl)-porphyrinato thallium(III), Tl(tpyp)CH_3. The observation of the ^{13}C resonance of the methyl ligand for this new and very similar complex is a challenging problem.

In this paper, the synthesis, the solution and solid-state ^{13}C CP/MAS NMR spectroscopic studies of the new complex, Tl(tpyp)CH_3, are reported which provides evidence for the methyl group being coordinated to the Tl atom.

EXPERIMENTAL

Preparation of Tl(tpyp)CH_3

The compound Tl(tpyp)(OAc) (50 mg) was dissolved in tetrahydrofuran 30 cm^3. A solution of methylmagnesium iodide, CH_3MgI, ($\approx$0.23 mol) in ether was added and the mixture was stirred for 4 h at 0°C. The reaction mixture was hydrolyzed with 30 cm^3 of water and extracted three times with methylene chloride (3 x 50 cm^3). The organic layer was washed with water until neutrality and then dried over Na_2SO_4. After filtration, the organic solution was taken to dryness under reduced pres-

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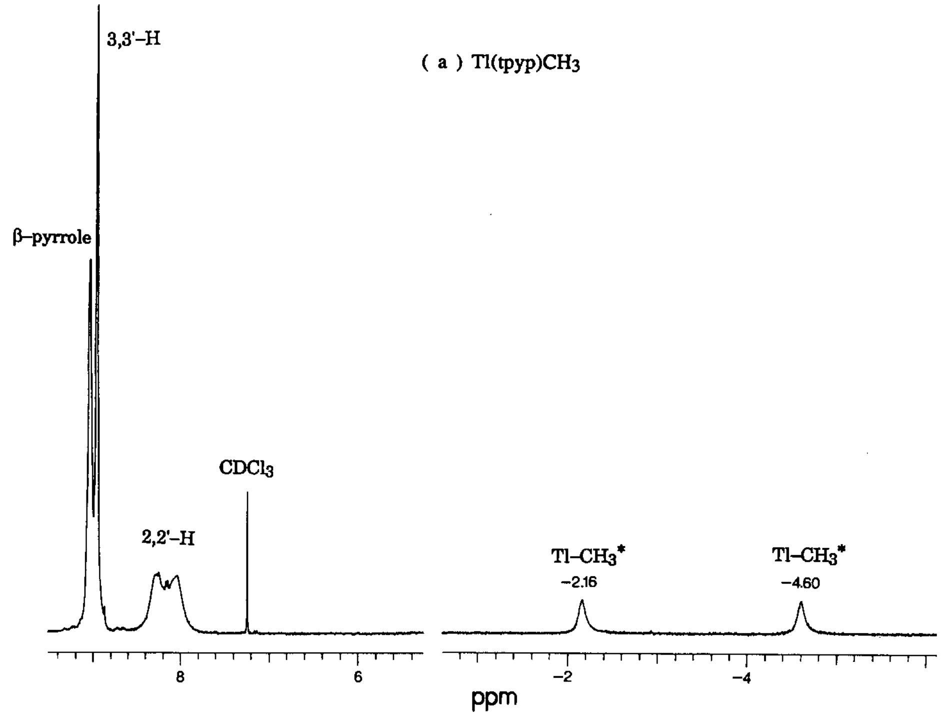
* Author to whom correspondence should be addressed.

sure by rotary evaporation. The obtained product was recrystallized from CH_2Cl_2–hexane yielding violet crystals (40.4 mg, 85%).

It was dissolved in $CDCl_3$ (99.8% from Aldrich) for NMR measurement at 24°C. ^1H NMR (shown in Fig. 1(a)): δ(ppm) −3.38 [d, CH_3—Tl, ^2J(Tl—^1H) = 731.9 Hz], 8.04 (s, 2-H) and 8.27 (s, 2′-H), 8.94 (m, 3 and 3′-H) and 9.03 [d, β-H, ^4J(Tl—^1H) = 4.4 Hz]. ^{13}C NMR (shown in Fig. 2(a) and Table 1): δ(ppm) 1.2 [d, Tl—*CH_3, ^1J(Tl—^{13}C) = 5750.8 Hz], 119.4 (m, C_{meso}), 129.5 (s, C_{-2} and $C_{-2'}$), 132.2 (s, C_β), 148.2 (s, C_{-3} and $C_{-3'}$), 149.5 (m, C_α), 150.4 (s, C_{-1}). The MS (FAB): [m/z, assignment, rel. intensity (%)] 836 $[M(^{205}Tl)]^+$, 5.32), 837 ($[M(^{205}Tl)+H]^+$, 10.72), 821 ($[M(^{205}Tl)-CH_3]^+$, 7.21).


(a) Tl(tpyp)CH3

(b) Tl(tpyp)13CH3

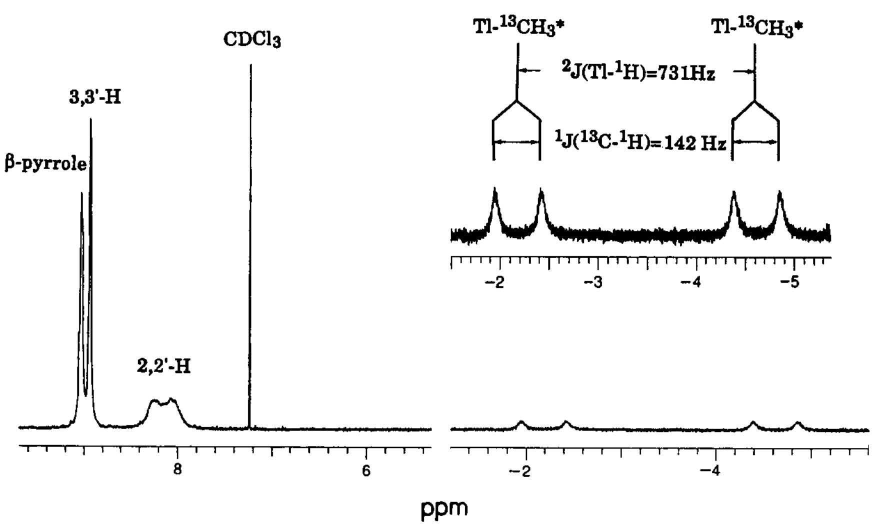


Fig. 1. 300 MHz ^1H NMR spectra in $CDCl_3$ at 24°C for (a) Tl(tpyp)CH_3 and (b) Tl(tpyp)$^{13}CH_3$.

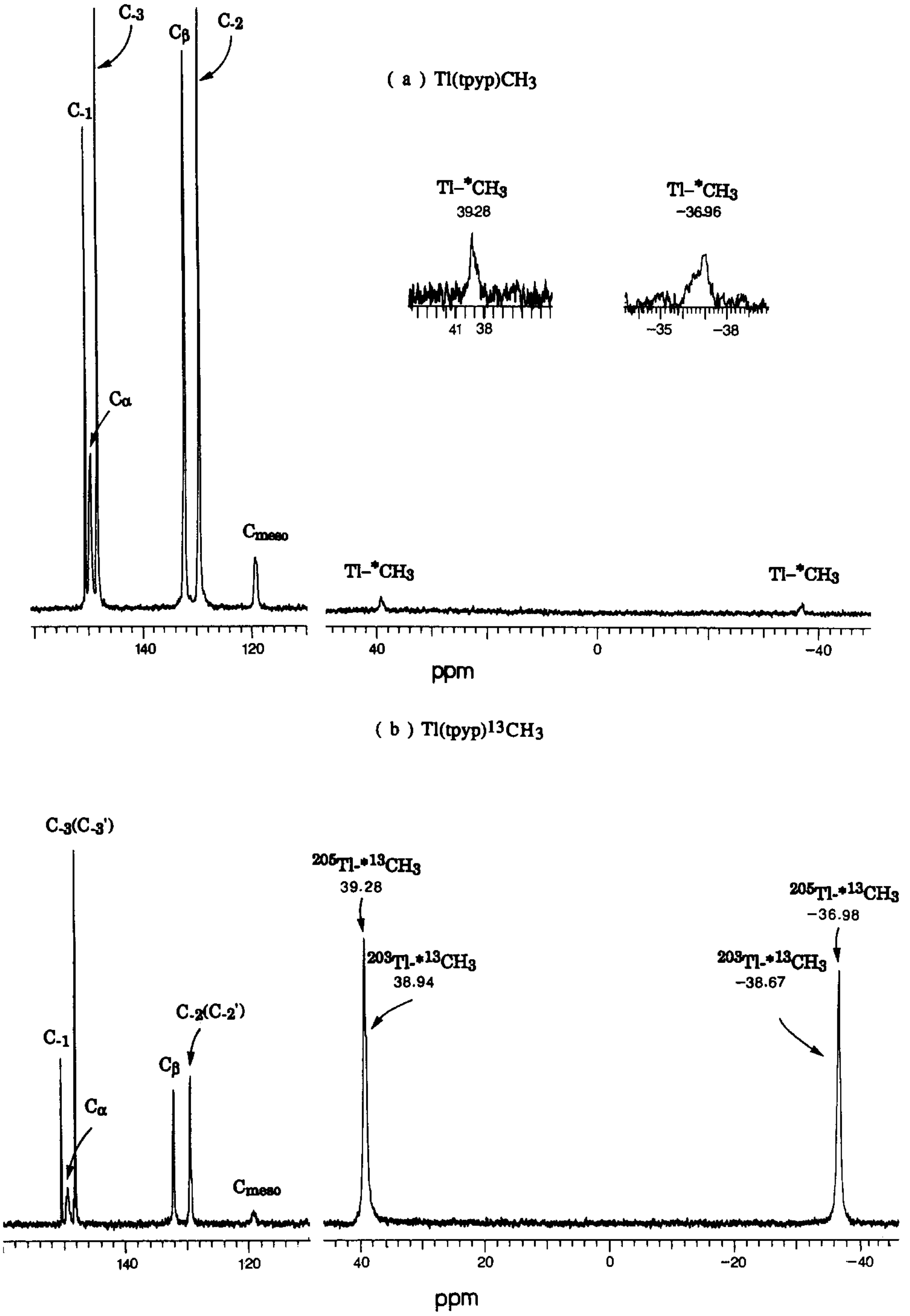


Fig. 2. 75.43 MHz ^{13}C broad band NMR spectra in $CDCl_3$ at 24°C for (a) Tl(tpyp)CH_3 and (b) Tl(tpyp)$^{13}CH_3$.

Preparation of Tl(tpyp)—$^{13}CH_3$

The ^{13}C-enriched Tl(tpyp)$^{13}CH_3$ was prepared by substituting CH_3MgI with $^{13}CH_3MgI$ in the preparation of Tl(tpyp)CH_3 as described previously. ^1H NMR (shown in Fig. 1(b)): δ(ppm) -3.39 [dd, $^{13}CH_3$—Tl, $^2J(Tl—^1H) = 731.3$ Hz, $^1J(^{13}C—^1H) = 142.4$ Hz]. ^{13}C NMR (shown in Fig. 2(b) and Table 1): δ(ppm) 1.2 [d, Tl—*$^{13}CH_3$, $^1J(^{205}Tl—^{13}C) = 5752.3$ Hz, $^1J(^{203}Tl—^{13}C) = 5703.3$ Hz]. All

Table 1. Comparison of ^{13}C chemical shifts (δ) and Tl—C coupling constant [J (Hz)] for the Tl(tpyp)$^{13}CH_3$ in $CDCl_3$ solvent and of Tl(tpyp)CH_3 between the solution (in $CDCl_3$ solvent) and solid-state NMR measurements at 24°C[a]

Medium and compound (carbon frequency)	C_{-1}	C_α	$C_{-3}(C_{-3'})$	C_β	$C_{-2}(C_{-2'})$	C_{meso}	Tl—CH_3	Doublet (ppm)	
								Downfield	Upfield
Solution Tl(tpyp)CH_3 (75.43 MHz)	150.4	149.5	148.2	132.2	129.5	119.4	1.2 ($^{205}Tl—^{13}C$ = 5750.8 Hz)	39.28	−36.96
Solution Tl(tpyp)$^{13}CH_3$ (75.43 MHz)	150.4	149.5	148.2	132.2	129.5	119.4	1.2 ($^{203}Tl—^{13}C$ = 5752.3 Hz) ($^{205}Tl—^{13}C$ = 5703.3 Hz)	39.28 38.94	−36.98 −36.67
Solid-state Tl(tpyp)CH_3 (50.33 MHz)		149.6 (singlet)		132.5 (multiplet)		119.4 (singlet)	Doublet with a upfield resonance at −56.7 ppm	–	−56.7

[a] Chemical shift in ppm relative to the centre line of $CDCl_3$ at 77.0 ppm at 24°C. Values in parentheses beneath are $^1J(Tl—^{13}C)$ coupling constants.

other ^1H and ^{13}C signals are similar to those reported for Tl(tpyp)CH_3 compound.

NMR spectra

^1H and ^{13}C NMR spectra were recorded at 300 and 75.43 MHz, respectively, using a Varian VXR-300 spectrometer at 24°C. Solid-state ^{13}C CP/MAS NMR spectra were recorded at 24°C at 50.33 MHz on a Bruker MSL-200 solid-state NMR spectrometer. Dry nitrogen gas was used to drive MAS rates of 2.5 kHz.

RESULTS AND DISCUSSION

Figure 2 shows the representative broad band ^{13}C spectra for Tl(tpyp)CH_3 and Tl(tpyp)$^{13}CH_3$ in $CDCl_3$ solutions at 24°C. The ^{13}C signal of $^{13}CH_3$ bonded to Tl(tpyp)$^{13}CH_3$ (shown in Fig. 2(b)) appears as two pairs of doublets at −36.98 and 39.28 ppm and −36.67 and 38.94 ppm for the outer and inner pairs, respectively. The outer pair arises from $^{205}Tl—^{13}C$ coupling (5752.3 Hz) and the inner one from $^1J(^{203}Tl—^{13}C)$ (5703.3 Hz). This is confirmed by noting that $^1J(^{205}Tl—^{13}C)/{}^1J(^{203}Tl—^{13}C) = 1.0086$, which is quite close to the theoretical value calculated from $\gamma(^{205}Tl)/\gamma(^{203}Tl) = 1.0098$. The outer pair shown in Fig. 2(b) is similar to the axial methyl carbon bonded to Tl(tpyp)CH_3 (shown in Fig. 2(a)), appearing as a doublet at −36.96 and 39.28 ppm with $^1J(^{205}Tl—^{13}C)$ coupling constant 5750.8 Hz.

The CP/MAS ^{13}C solid-state NMR spectra of Tl(tpyp)CH_3 is shown in Fig. 3 and Table 1. The major resonance of the CH_3 bonded to Tl(tpyp)CH_3 is observed as a doublet with an upfield resonance at −56.70 ppm and it is difficult to detect the downfield resonance.

By substituting $\delta = 1.2$ ppm and $^1J(^{205}Tl—^{13}C) = 5751.6$ Hz,[3] obtained from the axial methyl carbon of Tl(tpyp)CH_3 (shown in Fig. 2), into $1.2 \pm [5751.6/(2 \times 50.33)]$, the calculated doublet for the methyl carbon with a 50.33 MHz (carbon) frequency turned out to be −56.0 and 58.3 ppm in the solid-state ^{13}C CP/MAS NMR measurement. The calculated resonance at −56.0 ppm is quite close to the observed one at −56.7 ppm.

In summary, the solution ^{13}C of CH_3 bonded to Tl(tpyp)CH_3 appears as a doublet at 39.28 and −36.96 ppm (with 75.43 MHz frequency) and the solid-state ^{13}C CP/MAS NMR indicates the same doublet at 58.3 (calculated) and −56.7 ppm (with 50.33 MHz frequency) providing evidence that the methyl ligand is axially coordinated to the Tl atom.

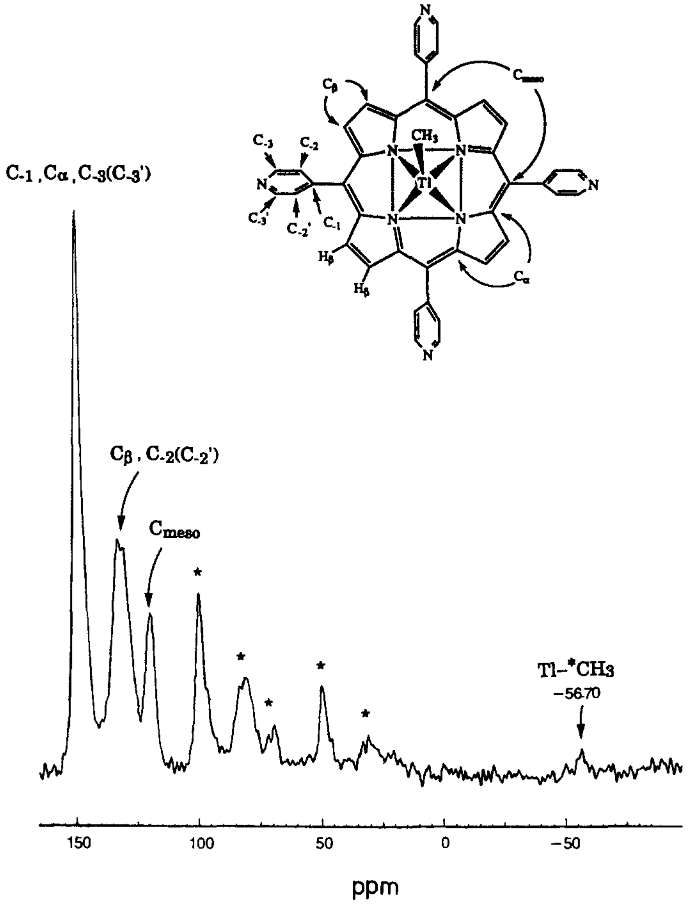


Fig. 3. High-resolution solid-state ^{13}C CP/MAS spectrum of $Tl(tpyp)CH_3$ at 50.33 MHz with spinning rate of 2.5 kHz at 24°C. Assignments: singlet at 149.6 ppm, C_{-1}, C_α, C_{-3} ($C_{-3'}$); multiplet at 132.5 ppm, C_β, C_{-2} ($C_{-2'}$); singlet at 119.4 ppm, C_{meso}; doublet at 58.3 (calculated), −56.70 ppm, Tl—CH_3. Spinning sidebands are labelled with an asterisk (*).

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3. 5751.6 Hz was calculated by 1/2(5750.8 ± 5752.3) from the data shown in Table 1.