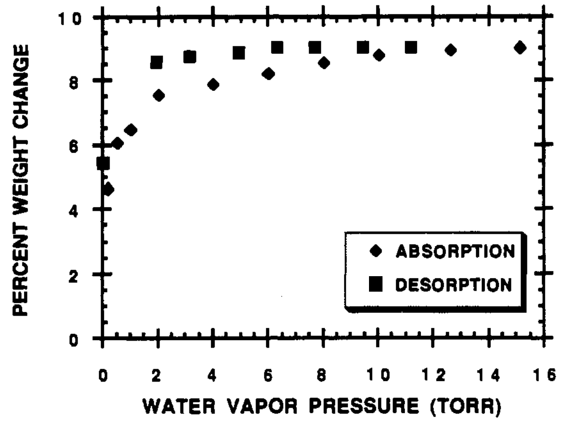

**Figure 2.** Water absorption isotherm for $(CH_3)_2NH_2[Mo_2O_2(PO_4)_2(H_2PO_4)]$ at 21 °C after the thermal decomposition of the ammonium cation (see text for conditions). The absorption isotherm is type I,[12] indicating the absorption of water into the micropores of the host lattice. The amount absorbed corresponds to filling ca. 25 vol % void space.

framework. The thermogravimetric analysis (TGA) of these materials under He shows a rather abrupt weight loss near 400–450 °C. The sharpness, as well as the relatively high temperature, of the TGA transition is not consistent with the expected thermal behavior of nonentrained methyl- or dimethylammonium cations. The IR absorptions associated with the organic cations disappear at temperatures corresponding to the TGA transition. There is no sharp weight loss in this temperature regime for the $Mo_2P_3O_{12}(OH)_2^-$ frameworks that contain no organics such as $Cs(H_3O)[Mo_2O_2(PO_4)_2(HPO_4)]$[10] and $H_3O[Mo_2O_2(PO_4)_2(H_2PO_4)]$.[10]

The structure of **2**, $(CH_3NH_3)[Mo_2O_2(PO_4)_2(H_2PO_4)]$, was examined with a single-crystal X-ray diffraction study.[11] Figure 1 shows the structure of **2** viewed both parallel and perpendicular to the $MoOPO_4$-like layers, and the interlamellar phosphate groups are obvious. There is a slight disorder of the $P(OH)_2$ portion of the $PO_2(OH)_2$ group about a crystallographic 2-fold axis. All of the Mo atoms are in the 5+ oxidation state and display the characteristic short Mo–O molybdenyl contacts (1.61 (1) Å).

While the analytical data discussed above leave no doubt that there are stoichiometric amounts of $MeNH_3^+$ cations in the molybdenum phosphate framework of **2**, we could find no trace of the cation in the crystal structure. All of the significant peaks in the final difference map (+1.70 to −1.41 $e{\cdot}Å^{-3}$) were near the Mo or P atoms. The simulation of the powder X-ray diffraction pattern of **2** generated from the single-crystal coordinates shows that the bulk material has the same structure found in the crystal used for the single-crystal X-ray diffraction study. The inability to locate the cations is probably due to a combination of three factors: (a) the tunnel in which the cation resides is larger than the cation, thus imposing little preferred orientation; (b) both ends of the $MeNH_3^+$ cation have essentially identical sizes and shapes, facilitating hydrogen bonds in one of two possible directions within the tunnel; (c) there is a 2-fold disorder in the interlamellar phosphate group, which is partially responsible for determining the size and shape of the tunnel, about a crystallographic 2-fold axis (Figure 1b).

To determine if these organic cations could be removed without collapsing the framework, i.e. if it were possible to generate any substantial internal micropore volume, we examined the water absorption isotherms at room temperature after the thermal decomposition of the organic cations. After a sample of $(CH_3)_2NH_2[Mo_2O_2(PO_4)_2(H_2PO_4)]$ was heated from 25 to 400 °C at a linear rate over 24 h under vacuum, the weight of water absorbed as a function of the water vapor pressure was measured. As shown in Figure 2, the shape of the absorption isotherm is type I[12] indicative of the absorption of the guest molecule into the micropores of the host and shows that the sample takes up 9–10 wt % water into the micropores in a nearly reversible manner. During this heating cycle the sample turned from yellow to brown but the powder X-ray diffraction measurements indicated that the sample was still crystalline although with somewhat broader peak widths indicative of a reduction in particle size or a slight reduction in crystalline order. Since the density of the Mo–P–O framework of this phosphate is >2.7 $g{\cdot}cm^{-1}$ and if the density of the adsorbed water is assumed to be less than or equal to 1 $g{\cdot}cm^{-1}$, then the absorbed water comprises ca. 25% of the volume of the hydrated sample. The water uptake, especially on the initial low-pressure absorption points, was rather slow, indicating that the water filled the internal volume of the crystals via a tortuous pathway.

In summary, a new class of molybdenum phosphates based on the $Mo_2O_2(PO_4)_2(H_2PO_4)^-$ framework can be easily prepared by the reaction of a $Mo^{5+}$ source in the presence of phosphoric acid. Unlike many other open framework solids, which yield a specific structure when hydrothermally prepared in the presence of a specific templating cation, the $Mo_2O_2(PO_4)_2(H_2PO_4)^-$ framework is very accommodating in terms of formation in the presence of cations of varying sizes and shapes. Absorption isotherms indicated it was possible, after decomposition of the entrained organic cation, to access essentially all of the internal volume of the solids when water is used as the probe molecule.

**Acknowledgment.** We are grateful to Professor A. Clearfield for sharing his related results on this system prior to publication and to Drs. J. W. Johnson and A. J. Jacobson for useful discussions.

**Supplementary Material Available:** Table S1, listing experimental crystallographic details, positional and thermal parameters, and bond distances and angles (9 pages); Table S2, listing calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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(10) R. Haushalter and L. Mundi, unpublished results.

(11) X-ray data for **2** (fw 540.86): monoclinic, space group *C*2 (No. 5), $a = 9.126$ (6), $b = 9.108$ (8), $c = 8.654$ (3) Å; $\beta = 114.06$ (4)°; $V = 656.8$ (8) $Å^3$; $Z = 2$. The calculated density is 2.735 $g{\cdot}cm^{-3}$, $\lambda = 0.71069$ Å, and $\mu = 22.99$ $cm^{-1}$ with transmission factors from 0.77 to 1.00. For 60 variables and 678 data with $I > 3.00\sigma(I)$, $R$ ($R_w$) = 0.061 (0.066). Maximum and minimum residual electron density = +1.70 and −1.41 $e{\cdot}Å^{-3}$.

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*Received August 3, 1990*

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# Novel Titanium(II) Amine Complexes $L_4TiCl_2$ [L = $^1/_2$ *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA), $^1/_2$ *N,N,N′*-Trimethylethylenediamine, Pyridine, $^1/_2$ 2,2′-Bipyridine]: Synthesis and Crystal Structure of Monomeric *trans*-$(TMEDA)_2TiCl_2$

Interest in the chemistry of divalent titanium has been stimulated by the very diverse aspects of its chemical reactivity, including activation of small molecules ($N_2$,[1] CO,[2] $CO_2$,[3] $H_2$[4]), reductive

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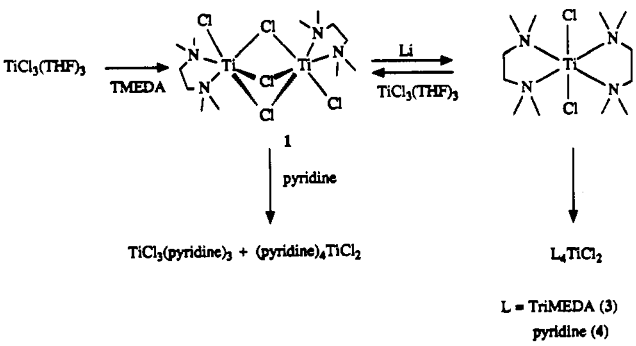
**Scheme I**



coupling of olefins[4] and acetylenes,[5] and a possible role played in Ziegler–Natta catalysis.[6] However, apart from the biscyclopentadienyl and related systems,[7] the chemistry of divalent titanium is poorly known and is limited to a few examples. Only three series of Ti(II) compounds have been characterized to date [$(dmpe)_2TiX_2$ (X = Cl,[8b] Me,[8a,b] $BH_4$[8a]), $(ArO)_2Ti(bpy)_2$,[9] and $(arene)TiCl_2(AlCl_3)_2$[10]], the other few ill-defined derivatives of Ti(II) being probably Ti(III) species or low-valent Ti complexes whose structures remain unknown.[11]

The lack of suitable Ti(II) starting compounds has probably been the limiting factor in the development of this chemistry. Recent results have shown that amines have an unexpected stabilizing effect on low-valent vanadium,[12] and due to the fact that these compounds are versatile starting materials[13] for studying the poorly known chemistry of V(II), we were especially interested in testing a similar synthetic strategy for the chemistry of low-valent group 4 transition metals. In this paper we wish to report the synthesis and crystallographic characterization of a novel class of *trans*-$Cl_2Ti(amine)_4$ complexes.

As illustrated in Scheme I the reduction of $TiCl_3(THF)_3$ with an excess of lithium in the presence of 6 equiv of TMEDA [TMEDA = *N,N,N',N'*-tetramethylethylenediamine] proceeded slowly at room temperature, initially forming a mixed-valence Ti(II)/Ti(III) species (**1**) as a very insoluble, air-sensitive, light brown solid. The solid dissolved within 2 days of stirring in the presence of metallic Li, forming a dark brown reddish solution from which air-sensitive, light violet crystals of *trans*-$(L)_4TiCl_2$ [L = $^1/_2$ TMEDA (**2**)] were obtained (yield 85%) after filtration, concentration, and cooling at −30 °C.[14]

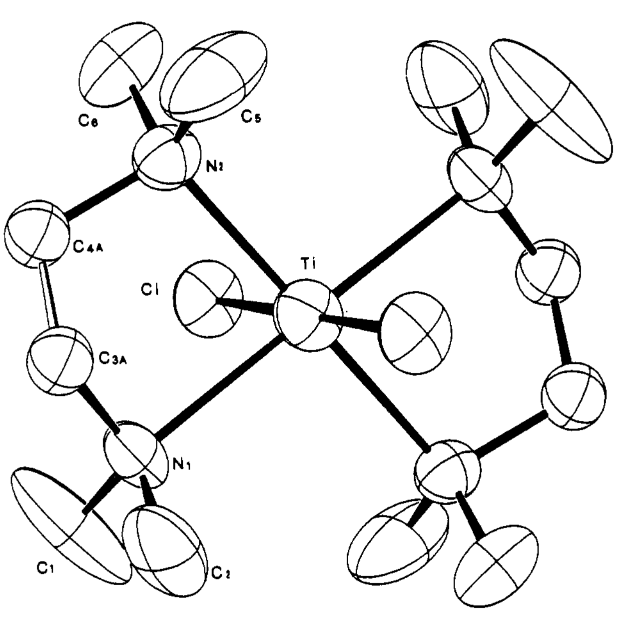
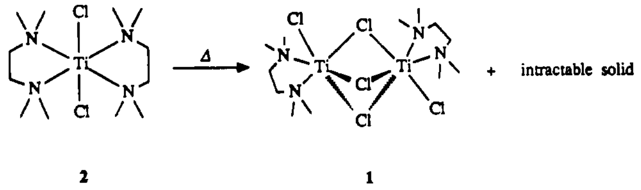


**Figure 1.** ORTEP drawing of **2**, showing the labeling scheme. Selected bond distances (Å) and angles (deg): Ti–Cl = 2.477 (2), Ti–N1 = 2.381 (7), Ti–N2 = 2.377 (7); Cl–Ti–N1 = 90.3 (2), Cl–Ti–N2 = 90.0 (2), N1–Ti–N2 = 79.2 (3).

**Scheme II**



The structure of the TMEDA adduct **2** has been demonstrated by X-ray analysis.[15] The molecule (Figure 1) possesses the same trans halide octahedral geometry previously observed for *trans*-$L_4VCl_2$[12] and *trans*-$(dmpe)_2TiCl_2$,[8b] with comparable values of the Ti–Cl distance [Ti–Cl = 2.477 (2) Å]. Conversely, the Ti–N distances are slightly longer than for the isostructural vanadium complex, probably as a result of a more efficient Ti–Cl π bonding. Conformational disorder was observed for the C3 and C4 atoms of the TMEDA ethylenic bridge.

The solution chemistry of **2** is characterized by a remarkable lability of the coordinated TMEDA ligands, allowing facile ligand replacement reactions with several amines, and formation of the corresponding *trans*-$Cl_2TiL_4$ derivatives [L = $^1/_2$ TriMEDA (**3**), pyridine (**4**), $^1/_2$, 2,2'-bipyridine, (**5**)] in crystalline form. The lability of the coordinated amine is probably responsible for the thermal instability of **2**–**4** toward the disproportionation to higher oxidation states. For instance, light violet crystals of **2** dissolve in both THF and toluene, yielding golden yellow solutions, which darken slowly at room temperature. The only identifiable reaction product was the mixed-valence species **1**, obtained as light brown

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(14) A red suspension of $TiCl_3(THF)_3$ (30.5 g, 0.082 mol) in THF (350 mL) was stirred with metallic lithium (1.9 g, 0.27 mol) in the presence of an excess of TMEDA (58 g, 0.497 mol). A brown insoluble microcrystalline material separated after 3 hours. The solid slowly dissolved during 48 h of stirring, forming a light violet crystalline solid. The mixture was diluted with THF (200 mL), filtered, and concentrated. Light violet crystals of **2** (24.8 g, 70 mmol, 85%) separated upon standing at low temperature (−30 °C).

(15) Crystal data for $C_{12}H_{32}Cl_2N_4Ti$ (**2**) at room temperature: monoclinic, space group *P*2/*n* with *a* = 7.984 (2) Å, *b* = 12.429 (2) Å, *c* = 9.385 (2) Å, $\beta$ = 97.49 (5)°, *V* = 923.4 (3) $Å^3$, *Z* = 2, and $d_{calcd}$ = 1.263 g $cm^{-3}$. Of 1459 unique reflections collected by using Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation ($2\theta_{max}$ = 44.8°), 966 with $I > 2.5\sigma(I)$ were used in the final refinement. *R* = 0.072, $R_w$ = 0.084, and GoF = 1.60. The highest residual peak in the final difference Fourier map was 0.500 e/$Å^3$. Due to the conformational disorder, atoms C3 and C4 were isotropically refined with an occupancy of 50%.

needles upon standing 24 h at room temperature (Scheme II). Very fast reaction was observed in boiling THF. A similar fate was observed for the pyridine complex **4**, whose royal blue solutions turned brown at room temperature within 24 h, forming olive green needles of $TiCl_3(py)_3$ upon cooling. Complex **3** decomposes only slowly in boiling toluene. Conversely, complex **5** and the mixed-valence species **1** are thermally robust and can be refluxed in THF for several days without observing any appreciable decomposition. That **1** is a Ti(II)/Ti(III) mixed-valence species has been indicated by its quantitative formation from $TiCl_3(THF)_3$ with $TiCl_2(TMEDA)_2$ (1:1 ratio). In accordance, chemical degradation of **1** with pyridine gave a mixture of olive green $TiCl_3(py)_3$ and royal blue $TiCl_2(py)_4$, which have been identified after fractional crystallization. While the 1:1 ratio has been confirmed by analytical data,[16] the dimeric structure has been tentatively assigned on the basis of the close similarities with the results obtained in the chemistry of analogous vanadium derivatives.[12b] Satisfactory elemental analyses have been obtained for all the complexes.[16]

The low value of the magnetic moment of **1**[16] is consistent with the presence of one unpaired electron per demeric unit. The ESR spectrum at X-band frequency at 295 K showed an isotropic spectrum characteristic of an octahedral species $S = 1/2$ ($g$ = 1.9384), and the $g$ anisotropy observed at 77 K ($g_\perp$ = 1.9485, $g_\parallel$ = 1.9264) confirmed that the complex has an axial symmetry.[17] These observations suggests also that a strong Ti···Ti interaction (probably bonding) may be present in complex **1**. With the only exception of **5**, which is diamagnetic, the other complexes are paramagnetic, with values of $\mu_{eff}$[16] as expected for a high-spin $d^2$ electronic configuration.

The general tendency of **2** to take part in aggregation reactions with $MX_n$ species (M = Al, Zn, Mg, Ln; X = Cl, Me, Et, OR, H) is at present under investigation in view of its relevance to Ziegler-Natta modeling studies.

**Acknowledgment.** This work has been supported by the Natural Sciences and Engineering Research Council of Canada (operating grant) and the Petroleum Research Fund, administered by the American Chemical Society. The Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) is gratefully acknowledged for providing a visiting scholarship (J.J.H.E.).

**Supplementary Material Available:** Text giving experimental details for the preparation of all the complexes and listings of crystallographic details, atomic positional and thermal parameters, anisotropic thermal parameters, and complete bond distances and angles (6 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(16) Analytical data are as follows. **1**: brown, 95%, $\mu_{eff}$ = 0.75 $\mu_B$ per Ti atom. Anal. Calcd (found) for $C_{12}H_{32}N_4Cl_5Ti_2$: C, 28.48 (28.87); H, 6.33 (6.28); N, 11.07 (10.52); Cl, 35.11 (34.97); Ti, 18.99 (18.45). **2**: light violet, 68%, $\mu_{eff}$ = 2.64 $\mu_B$. Anal. Calcd (found) for $C_{12}H_{32}N_4Cl_2Ti$: C, 40.99 (40.77); H, 9.11 (9.06); N, 15.94 (15.87); Cl, 20.21 (20.21); Ti, 13.66 (13.48). **3**: pink, 75%, $\mu_{eff}$ = 2.57 $\mu_B$. Anal. Calcd (found) for $C_{10}H_{28}N_4Cl_2Ti$: C, 37.15 (37.01); H, 8.67 (8.55); N, 17.33 (17.27); Cl, 21.98 (21.89); Ti, 14.86 (14.83). **4**: royal blue, 80%, $\mu_{eff}$ = 2.67 $\mu_B$. Anal. Calcd (found) for $C_{20}H_{20}N_4Cl_2Ti$: C, 55.17 (55.14); H, 4.59 (4.49); N, 12.87 (12.84); Cl, 16.32 (16.24); Ti, 11.03 (10.90). **5**: deep blue, 84%, diamagnetic. Anal. Calcd (found) for $C_{20}H_{18}N_4Cl_2Ti$: C, 55.42 (55.31); H, 4.16 (4.09); N, 12.93 (12.88); Cl, 16.39 (16.27); Ti, 11.08 (11.01).

(17) ESR spectra of **1** were recorded in the solid state by using the following instrument settings: $\nu$ = 9.34 GHz; microwave power 2 mW; field modulation amplitude 0.1 G.

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*Received September 26, 1990*

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## Activated Molybdenum-Molybdenum Quadruple Bonds. 2. First Example of Alkyne Additions to Metal-Metal Quadruple Bonds

Quadruply-bonded dimetal complexes have been known for more than 26 years;[1] however, their use in activation of alkynes and other small molecules has received little attention.[2-6] Previously, we reported that ethylenediamine (en) solutions of $Mo_2(O_2CMe)_4$ (**1**) produced an "activated" quadruply-bonded dimolybdenum dication, $[Mo_2(en)_4(O_2CMe)_2]^{2+}[(O_2CMe)_2]^{2-}\cdot en$, that showed unusual reactivity toward a variety of inorganic and organic substrates.[7,8] As a continuation of these studies, we describe here the first alkyne derivatives of a metal-metal quadruply-bonded complex.[9] The alkyne ligands in these compounds are thermally hydrogenated and extruded as alkenes via an unusual amine-to-alkyne hydrogen-transfer reaction.

Addition of the terminal aryl alkynes $4\text{-}RC_6H_4C{\equiv}CH$ (R = H, Me, *i*-Pr) to en solutions of $Mo_2(O_2CMe)_4$ at room temperature affords the alkyne adducts **2** (R = H), **3** (R = Me), and **4** (R = *i*-Pr) of empirical formula $[Mo_2(\mu\text{-}4\text{-}RC_6H_4CCH)(\mu\text{-}O_2CMe)(en)_4{}^{3+}][O_2CMe^-)_3]\cdot 2en$. The three compounds are formed in two isomeric configurations, **a** and **b**, in approximately a 1:1 ratio (eq 1), as determined by $^1H$ and $^{13}C$ NMR spectroscopy.[10] Newman projections of the two isomers viewed down the Mo-Mo bonds are shown as follows:

$$Mo_2(O_2CMe)_4 + 4\text{-}RC_6H_4C{\equiv}CH \xrightarrow{en} \mathbf{a} + \mathbf{b} \qquad (1)$$

R = H, **2a** and **2b**
R = Me, **3a** and **3b**
R = *i*-Pr, **4a** and **4b**

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(10) To an orange-red solution of **1** (90 mg, 0.21 mmol) in en (anhydrous, 2 mL) was added $4\text{-}MeC_6H_4C{\equiv}CH$ (29 mg, 0.25 mmol), producing an immediate color change to dark red. After several days, red-purple crystals of **3a** and **3b** coprecipitated and were dried in vacuo (74 mg; 44%, based on **1**). The same procedure is used for the synthesis of **2a**, 2b, **3a**, and **3b**. Selected NMR data for an appropriate equimolar mixture of **2a** and **2b** are as follows. $^1H$ NMR (DMSO-$d_6$, 25 °C): $\delta$ 8.44 (s, 1 H), 7.13 (s, 1 H) ($C_6H_5CC\mathit{H}$); $\delta$ 7.34 (t, $J$ = 7.5 Hz, 2 H, meta); $\delta$ 7.22 (d, $J$ = 7.7 Hz, 2 H, ortho); $\delta$ 7.13 (t, $J$ = 7.0 Hz, 1 H, para); $\delta$ 7.26 (t, $J$ = 7.6 Hz, 2 H, meta); $\delta$ 7.02 (t, $J$ = 7.1 Hz, 1 H, para); $\delta$ 6.99 (d, $J$ = 8.0 Hz, 2 H, ortho) ($C_6\mathit{H}_5CCH$). $^{13}C$ NMR (DMSO-$d_6$, 25 °C): $\delta$ 141.5, 127.2 ($C_6H_5C\mathit{C}H$). Selected spectroscopic data for an approximate equimolar mixture of **3a** and **3b** are as follows. $^1H$ NMR (DMSO-$d_6$, 25 °C): $\delta$ 8.40 (s, 1 H), 7.10 (s, 1 H) ($4\text{-}MeC_6H_4CC\mathit{H}$); $\delta$ 7.16 (d, $J$ = 8 Hz, 2 H), 7.12 (d, $J$ = 8 Hz, 2 H), 7.09 (d, $J$ = 8 Hz, 2 H), 6.90 (d, $J$ = 8 Hz, 2 H) ($4\text{-}MeC_6\mathit{H}_4CCH$); $\delta$ 2.39 (s, 3 H), 2.34 (s, 3 H) ($4\text{-}\mathit{Me}C_6H_4CCH$). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$): $\delta$ 141.6, 127.3 ($4\text{-}MeC_6H_4C\mathit{C}H$). Molar conductivity (DMSO, 25 °C): 32 $\Omega^{-1}$ $cm^2$ $M^{-1}$. Anal. Calcd for $C_{29}H_{68}N_{12}O_8Mo_2$: C, 38.50; H, 7.57; N, 18.58. Found: C, 38.64; H, 7.85; N, 19.68. Selected NMR data for an approximate equimolar mixture of **4a** and **4b** are as follows. $^1H$ NMR (DMSO-$d_6$, 25 °C): $\delta$ 8.48 (s, 1 H) ($4\text{-}i\text{-}PrC_6H_4CC\mathit{H}$); $\delta$ 7.2 (m, 7 H) ($4\text{-}i\text{-}PrC_6\mathit{H}_4CCH$ and [$4\text{-}i\text{-}PrC_6H_4CC\mathit{H}$]; $\delta$ 6.93 (d, $J$ = 8 Hz, 2 H) ($4\text{-}i\text{-}PrC_6\mathit{H}_4CCH$); $\delta$ 1.22 (d, $J$ = 9 Hz, 6 H), 1.20 (d, $J$ = 9 Hz, 6 H) ($4\text{-}i\text{-}\mathit{Pr}C_6H_4CCH$). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$): $\delta$ 25.4, 23.9 ($4\text{-}i\text{-}\mathit{Pr}C_6H_4CCH$).

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