

# One-Pot Synthesis of Metal Primary Phosphine Complexes from O=PCl<sub>2</sub>R or PCl<sub>2</sub>R. Isolation and Characterization of Primary Alkylphosphine Complexes of a Metalloporphyrin

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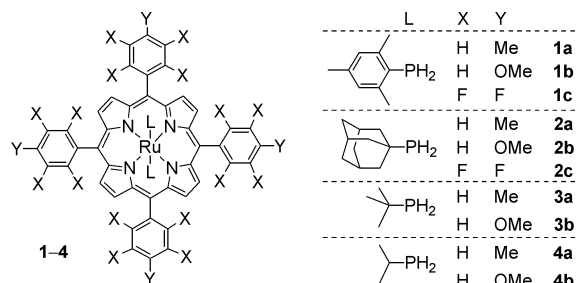
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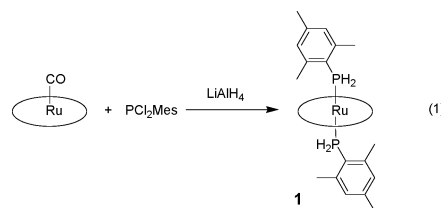
Treatment of [Ru<sup>II</sup>(Por)(CO)] [Por = porphyrinato(2-)] and O=PCl<sub>2</sub>R [R = Ad (adamantyl), Bu<sup>t</sup>, Bu<sup>sec</sup>] or PCl<sub>2</sub>Mes (Mes = mesityl) with LiAlH<sub>4</sub> afforded primary alkyl- and arylphosphine complexes [Ru<sup>II</sup>(Por)(PH<sub>2</sub>R)<sub>2</sub>], which have been isolated in pure form and characterized by <sup>1</sup>H NMR, <sup>31</sup>P NMR, IR, and UV–vis spectroscopy and mass spectrometry. The structures of [Ru<sup>II</sup>(TTP)(PH<sub>2</sub>Ad)<sub>2</sub>] and [Ru<sup>II</sup>(F<sub>20</sub>-TPP)(PH<sub>2</sub>Mes)<sub>2</sub>] were determined by X-ray crystallography.

Primary phosphine complexes of transition metals are of interest in metal-mediated P–H bond functionalizations,<sup>1–3</sup> phosphido/phosphinidene formation,<sup>4,5</sup> and materials science.<sup>6,7</sup> The known methods of preparing these metal complexes require the use of preisolated primary phosphines,<sup>8</sup> which are often highly air-sensitive toxic liquids and exhibit an intense unpleasant odor.<sup>9</sup> By treating PH<sub>2</sub>Ph with [Ru<sup>II</sup>(Por)(CO)] [Por = porphyrinato(2-)], we previously isolated several primary arylphosphine complexes of ruthenium porphyrins.<sup>10</sup> In the course of our studies on primary

phosphine complexes of metalloporphyrins, we found that O=PCl<sub>2</sub>R [R = Ad (adamantyl), Bu<sup>t</sup>, Bu<sup>sec</sup>] and PCl<sub>2</sub>Mes (Mes = mesityl), the typical precursors for the preparation of primary phosphines, can be directly used to prepare metal primary phosphine complexes.



Treatment of a solution of [Ru<sup>II</sup>(Por)(CO)] and PCl<sub>2</sub>Mes in diethyl ether with excess LiAlH<sub>4</sub> at 0 °C for 30 min led to the formation of primary arylphosphine complexes [Ru<sup>II</sup>(Por)(PH<sub>2</sub>Mes)<sub>2</sub>] (Por = TTP, <sup>11a</sup> **1a**; 4-MeO-TPP, <sup>11b</sup> **1b**; F<sub>20</sub>-TPP, <sup>11c</sup> **1c**). After decomposition of unreacted LiAlH<sub>4</sub> with methanol followed by filtration and recrystallization, **1a–c** were isolated in up to 65% yield (reaction 1).



When [Ru<sup>II</sup>(Por)(CO)] and O=PCl<sub>2</sub>R (R = Ad, Bu<sup>t</sup>) were treated with excess LiAlH<sub>4</sub> under similar conditions, primary alkylphosphine complexes [Ru<sup>II</sup>(TTP)(PH<sub>2</sub>R)<sub>2</sub>] (R = Ad, **2a**;

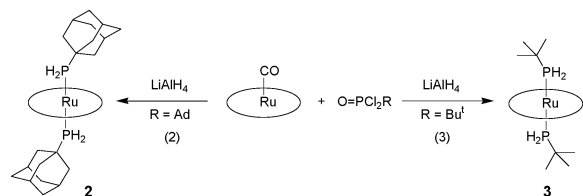
(10) Xie, J.; Huang, J.-S.; Zhu, N.; Zhou, Z.-Y.; Che, C.-M. *Chem.–Eur. J.* **2005**, *11*, 2405.

(11) (a) TTP = *meso*-tetrakis(*p*-tolyl)porphyrinato(2-). (b) 4-MeO-TPP = *meso*-tetrakis(*p*-methoxyphenyl)porphyrinato(2-). (c) F<sub>20</sub>-TPP = *meso*-tetrakis(*p*-pentafluorophenyl)porphyrinato(2-).

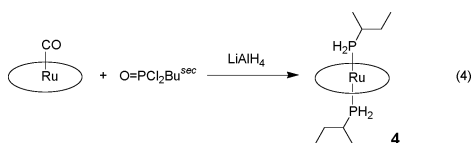
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- (1) Malisch, W.; Hirth, U.-A.; Grün, K.; Schmeusser, M.; Fey, O.; Weis, U. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2500.
- (2) Douglass, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10221.
- (3) Malisch, W.; Klüpfel, B.; Schumacher, D.; Nieger, M. *J. Organomet. Chem.* **2002**, *661*, 95.
- (4) Zwick, B. D.; Dewey, M. A.; Knight, D. A.; Buhro, W. E.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 2673.
- (5) Termaten, A. T.; Aktas, H.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Organometallics* **2003**, *22*, 1827.
- (6) Lewkebandara, T. S.; Proscia, J. W.; Winter, C. H. *Chem. Mater.* **1995**, *7*, 1053.
- (7) Scheper, J. T.; Jayaratne, K. C.; Liable-Sands, L. M.; Yap, G. P. A.; Rheingold, A. L.; Winter, C. H. *Inorg. Chem.* **1999**, *38*, 4354.
- (8) Tungsten complexes of PH<sub>2</sub>Cl and PH<sub>2</sub>F can be prepared from [W(CO)<sub>5</sub>{PH<sub>2</sub>(NEt<sub>2</sub>)}]. See: Mercier, F.; Mathey, F.; Afiong-Akpan, C.; Nixon, J. F. *J. Organomet. Chem.* **1988**, *348*, 361. Sequential treatment of [W(CO)<sub>5</sub>(PH<sub>3</sub>)] with <sup>n</sup>BuLi and ClH<sub>2</sub>B•NMe<sub>3</sub> gave [W(CO)<sub>5</sub>(PH<sub>2</sub>BH<sub>2</sub>•NMe<sub>3</sub>)], as reported in: Vogel, U.; Hoemensch, P.; Schwan, K.-C.; Timoshkin, A. Y.; Scheer, M. *Chem.–Eur. J.* **2003**, *9*, 515.
- (9) Brynda, M. *Coord. Chem. Rev.* **2005**, *249*, 2013.

Bu<sup>t</sup>, **3a**), [Ru<sup>II</sup>(4-MeO-TPP)(PH<sub>2</sub>R)<sub>2</sub>] (R = Ad, **2b**; Bu<sup>t</sup>, **3b**), and [Ru<sup>II</sup>(F<sub>20</sub>-TPP)(PH<sub>2</sub>Ad)<sub>2</sub>] (**2c**) were isolated in up to 70% yield (reactions 2 and 3). To the best of our knowledge, **2a,b** and **3a,b** are the first examples of (i) primary alkylphosphine complexes of a metalloporphyrin and (ii) primary alkylphosphine complexes of Ru. Prior to this work, a few primary arylphosphine<sup>10</sup> and alkynylphosphine<sup>12</sup> complexes of ruthenium porphyrins and non-porphyrin primary arylphosphine complexes of Ru (such as *trans*-[Ru<sup>II</sup>Cl<sub>2</sub>(PH<sub>2</sub>Ph)<sub>4</sub>])<sup>13</sup> were reported.



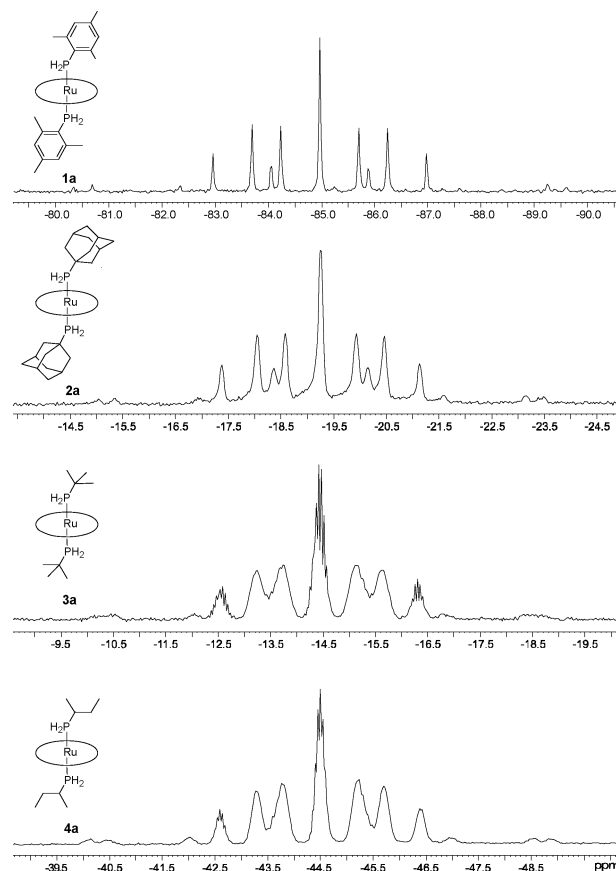
Transition-metal complexes of acyclic, primary alkylphosphines containing  $\alpha$ -C–H bonds are scarce.<sup>9</sup> Only M<sup>II</sup>X<sub>2</sub>·PH<sub>2</sub>Et (M = Co, Zn) and Co<sup>II</sup>X<sub>2</sub>·2PH<sub>2</sub>Et bearing such phosphine ligands are known.<sup>14</sup> To examine the coordination behavior of this type of primary alkylphosphine toward ruthenium porphyrins, we treated a solution of [Ru<sup>II</sup>(Por)(CO)] and O=P(Cl)<sub>2</sub>Bu<sup>sec</sup> with excess LiAlH<sub>4</sub> under conditions similar to those for reactions 1–3, which led to the isolation of [Ru<sup>II</sup>(Por)(PH<sub>2</sub>Bu<sup>sec</sup>)<sub>2</sub>] (Por = TTP, **4a**; 4-MeO-TPP, **4b**) in up to 65% yield (reaction 4).



Complexes **1–4** can also be prepared by treatment of [Ru<sup>II</sup>(Por)(CO)] with excess PH<sub>2</sub>Mes, PH<sub>2</sub>Ad, PH<sub>2</sub>Bu<sup>t</sup>, and PH<sub>2</sub>Bu<sup>sec</sup>, respectively, in dichloromethane. However, this method is less favorable because PH<sub>2</sub>Mes, PH<sub>2</sub>Ad, PH<sub>2</sub>Bu<sup>t</sup>, and PH<sub>2</sub>Bu<sup>sec</sup> are not commercially available and are more difficult to handle than the corresponding O=P(Cl)<sub>2</sub>R or PCl<sub>2</sub>Mes.

The preparation of **1–4** from the reaction of [Ru<sup>II</sup>(Por)(CO)] and O=P(Cl)<sub>2</sub>R/PCl<sub>2</sub>R with LiAlH<sub>4</sub> apparently involves in situ formation of primary phosphines PH<sub>2</sub>R, which react with [Ru<sup>II</sup>(Por)(CO)] to give the desired complexes. Evidence for this includes the following: (i) PH<sub>2</sub>R can be prepared from the reaction of O=P(Cl)<sub>2</sub>R or PCl<sub>2</sub>R with LiAlH<sub>4</sub>, (ii) the carbonyl group in [Ru<sup>II</sup>(Por)(CO)] could readily be replaced by PH<sub>2</sub>R but not by O=P(Cl)<sub>2</sub>R or by PCl<sub>2</sub>R, and (iii) [Ru<sup>II</sup>(Por)(CO)] exhibits no appreciable reaction with LiAlH<sub>4</sub> under conditions similar to those used for the preparation of **1–4**.

Complexes **1–4** are diamagnetic, showing the signals of primary phosphine axial ligands as a sharp singlet at  $\delta \sim -85$



**Figure 1.** <sup>31</sup>P NMR spectra of [Ru<sup>II</sup>(TTP)(PH<sub>2</sub>R)<sub>2</sub>] (R = Mes, **1a**; Ad, **2a**; Bu<sup>t</sup>, **3a**; Bu<sup>sec</sup>, **4a**) in CDCl<sub>3</sub>. After <sup>1</sup>H decoupling, only a sharp singlet was observed for each complex.

(**1a–c**),  $-20$  (**2a–c**),  $-14$  (**3a,b**), and  $-44$  ppm (**4a,b**) in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra. IR measurements revealed that **1–4** show their oxidation state marker bands<sup>10</sup> at 1002–1004 cm<sup>-1</sup>, similar to those of [Ru<sup>II</sup>(Por)(PH<sub>2</sub>Ph)<sub>2</sub>].<sup>10</sup> The UV–vis spectra of **2–4** exhibit Soret and  $\beta$  bands at  $\sim 428$  and  $\sim 520$  nm, respectively; the latter are blue-shifted from those of **1** and [Ru<sup>II</sup>(Por)(PH<sub>2</sub>Ph)<sub>2</sub>]. In the positive-ion FAB mass spectra, the parent-ion cluster peaks, together with the peaks of fragments [Ru<sup>II</sup>(Por)(PH<sub>2</sub>R)]<sup>+</sup> and [Ru<sup>II</sup>(Por)]<sup>+</sup>, can be observed for all of these primary phosphine complexes of metalloporphyrins.

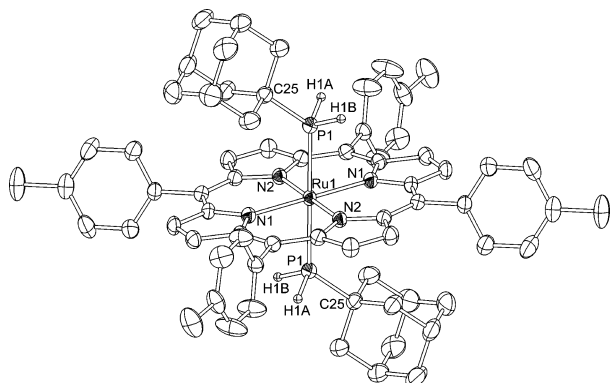
Previous work<sup>10</sup> has demonstrated that complexes [Ru<sup>II</sup>(Por)(PH<sub>2</sub>Ph)<sub>2</sub>] each exhibit a characteristic set of 15 signals (9 of which are prominent) in the <sup>31</sup>P NMR spectra, due mainly to strong couplings between the <sup>31</sup>P nuclei of the *trans* PH<sub>2</sub>Ph ligands (<sup>2</sup>J<sub>P,P</sub>  $\approx 500$  Hz) and between adjacent <sup>1</sup>H and <sup>31</sup>P nuclei of each PH<sub>2</sub>Ph ligand (<sup>1</sup>J<sub>P,H</sub>  $\approx 330$  Hz). Similar <sup>31</sup>P NMR spectral patterns were observed for **1a–c**; the spectrum of **1a** is depicted in Figure 1. The <sup>31</sup>P NMR signal patterns of **2a–c** closely resemble those of [Ru<sup>II</sup>(Por)(PH<sub>2</sub>Ph)<sub>2</sub>] and **1a–c** (see the spectrum of **2a** in Figure 1). Somewhat more complicated <sup>31</sup>P NMR spectra were observed for **3a,b** and **4a,b** (Figure 1), but the main patterns of the spectra are similar to those of **2a–c**. Approximate <sup>2</sup>J<sub>P,P</sub> and <sup>1</sup>J<sub>P,H</sub> values for **1–4** derived from NMR simulation are given in the Supporting Information.

The <sup>1</sup>H NMR spectra of **1–3**, like those of [Ru<sup>II</sup>(Por)(PH<sub>2</sub>Ph)<sub>2</sub>],<sup>10</sup> characteristically show their PH<sub>2</sub> resonances as a set

(12) Stulz, E.; Maue, M.; Scott, S. M.; Mann, B. E.; Sanders, J. K. M. *New J. Chem.* **2004**, *28*, 1066.

(13) Blake, A. J.; Champness, N. R.; Forder, R. J.; Frampton, C. S.; Frost, C. A.; Reid, G.; Simpson, R. H. *J. Chem. Soc., Dalton Trans.* **1994**, 3377.

(14) Hatfield, W. E.; Yoke, J. T. *Inorg. Chem.* **1962**, *1*, 470.



**Figure 2.** ORTEP drawing for  $[\text{Ru}^{\text{II}}(\text{TTP})(\text{PH}_2\text{Ad})_2]$  (**2a**) with omission of C–H hydrogen atoms (thermal ellipsoid probability: 30%).

of six peaks centered at  $\delta \sim -0.7$  (**1a–c**),  $-2.1$  (**2a–c**), and  $-1.9$  ppm (**3a,b**) (see, for example, Figures S1 and S2 in the Supporting Information). For **4a,b**, their  $\text{PH}_2$  signals appear in the same region as some of the  $\text{Bu}^{\text{sec}}$  groups, resulting in significant signal overlaps; however, five of the six peaks of  $\text{PH}_2$  are still discernible (see the spectrum of **4a** in Figure S2 in the Supporting Information). A notable difference between the  $\text{PH}_2$  signal patterns of **4** and those of **1–3** is that the most intense peaks appear as multiplets in the former but as singlets in the latter, apparently owing to the more complicated spin systems in **4**.

Complexes **2–4** exhibit their pyrrolic proton ( $\text{H}_\beta$ ) resonances as a sharp singlet at  $\delta$  8.28–8.34 ppm, similar to the  $\text{H}_\beta$  chemical shifts of  $\delta$  8.24–8.26 ppm for **1a–c** and  $\delta$  8.24–8.28 ppm for  $[\text{Ru}^{\text{II}}(\text{Por})(\text{PH}_2\text{Ph})_2]$ .<sup>10</sup> This indicates that the primary alkyl- and arylphosphine axial ligands have similar influences on the chemical shifts of the  $\text{H}_\beta$  signals.

The  $\beta$ -C–H proton resonances of the primary alkylphosphine axial ligands appear as a singlet at  $\delta \sim -1.27$  ppm for **2a–c**, a multiplet centered at  $\delta -1.41$  ppm for **3a,b**, and two multiplets centered at  $\delta \sim -0.98$  and  $-1.50$  ppm, respectively, for **4a,b** ( $\text{CH}_2$ , note the diastereotopic nature of these protons in **4**). Complexes **4a,b**, the unique primary phosphine complexes of metalloporphyrins whose primary phosphine ligands contain  $\alpha$ -C–H bonds, show the signals of such C–H bonds as a multiplet with  $\delta \sim -1.88$  ppm.

$^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , and  $^{31}\text{P}$  NMR measurements revealed that **1–4** exhibit no detectable dissociation in a  $\text{CDCl}_3$  solution at room temperature. This observation, along with the successful isolation of **1–4**, reflects a high affinity of ruthenium(II) porphyrins for primary aryl- and alkylphosphines. Complexes **1–4** can even exist in a chloroform solution open to air at room temperature for hours, although decomposition to unidentified species occurred for the solutions upon prolonged standing. In the solid state, the complexes can be stored in air for several days.

We have determined the crystal structures of **1c** (Figure S3 in the Supporting Information) and **2a**· $2\text{C}_5\text{H}_{12}$  (Figure 2; selected bond distances and angles are given in Table S1 in the Supporting Information).<sup>15</sup> The molecules of the two complexes have a crystallographic center of symmetry; their porphyrin rings are essentially planar, with mean displacements of 0.0443 Å (**1c**) and 0.0168 Å (**2a**) from the least-squares planes.

The structure of **1c** features a Ru1–P1 distance of 2.358(20) Å, similar to the average value [2.3603(10) Å] of the corresponding distances in  $[\text{Ru}(\text{F}_{20}\text{-TPP})(\text{PH}_2\text{Ph})_2]$ .<sup>10</sup> However, the Ru–P–C angle [120.41(11)°] and the dihedral angle between the phosphine phenyl and porphyrin ring planes (28.8°) in **1c** are considerably smaller than those in  $[\text{Ru}(\text{F}_{20}\text{-TPP})(\text{PH}_2\text{Ph})_2]$  (average values: 129.11(11)° and 81.6°, respectively),<sup>10</sup> probably owing to the bulky mesityl group in  $\text{PH}_2\text{Mes}$  relative to the phenyl group in  $\text{PH}_2\text{Ph}$ . A smaller dihedral angle between the phosphine phenyl and porphyrin ring planes in **1c** is favored not only for reducing the steric hindrance between the porphyrin ring and the 2,6-dimethyl groups of  $\text{PH}_2\text{Mes}$  ligands but also for increasing the  $\pi$ – $\pi$  interaction between the phosphine phenyl group and porphyrin ring (such a  $\pi$ – $\pi$  interaction would reduce the Ru–P–C angle).

In the crystal structure of **2a**, a Ru–P distance of 2.349(26) Å was observed, which is similar to that of **1c**. The Ru–P–C angle in **2a** is 128.34(10)°, larger than that in **1c** but slightly smaller than that in  $[\text{Ru}^{\text{II}}(\text{F}_{20}\text{-TPP})(\text{PH}_2\text{Ph})_2]$ . A larger Ru–P–C angle in **2a** (as compared to **1c**) could be rationalized by the presence of the adamantyl moiety, which is bulkier than the mesityl group, and by the absence of a  $\pi$ – $\pi$  interaction between the phosphine and porphyrin ring in **2a**. The decrease in the Ru–P–C angle on going from  $[\text{Ru}^{\text{II}}(\text{F}_{20}\text{-TPP})(\text{PH}_2\text{Ph})_2]$  to **2a** might arise from the decrease in steric hindrance along the  $\text{F}_{20}\text{-TPP} \rightarrow \text{TTP}$  ligand.

In conclusion, we have demonstrated a one-pot synthesis of metal primary phosphine complexes from user-friendly  $\text{O}=\text{PCl}_2\text{R}$  and  $\text{PCl}_2\text{R}$  and isolated several primary alkylphosphine complexes of a metalloporphyrin. In view of the stability of  $[\text{Ru}^{\text{II}}(\text{Por})(\text{PH}_2\text{R})_2]$  (such as **1–4** and the remarkably stable  $[\text{Ru}^{\text{II}}(\text{F}_{20}\text{-TPP})(\text{PH}_2\text{Ph})_2]$  reported earlier<sup>10</sup>), the “[ $\text{Ru}^{\text{II}}(\text{Por})(\text{CO})$ ] +  $\text{O}=\text{PCl}_2\text{R}/\text{PCl}_2\text{R}$  +  $\text{LiAlH}_4$ ” system could serve as a useful means of providing stable “solidified” forms of simple primary phosphines for easier storage and selective functionalization, which is a complement to the stabilization of primary phosphines by significantly altering their structures (such as adding steric hindrance/changing electronic properties through covalent bonds).<sup>9</sup>

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**Supporting Information Available:** Experimental details, Table S1, Figures S1–S3, and CIF files for  $[\text{Ru}^{\text{II}}(\text{F}_{20}\text{-TPP})(\text{PH}_2\text{Mes})_2]$  (**1c**) and  $[\text{Ru}^{\text{II}}(\text{TTP})(\text{PH}_2\text{Ad})_2] \cdot 2\text{C}_5\text{H}_{12}$  (**2a**· $2\text{C}_5\text{H}_{12}$ ). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) Crystal data for **1c**: monoclinic,  $P2_1/c$ ,  $a = 11.103(2)$  Å,  $b = 11.570(2)$  Å,  $c = 21.840(4)$  Å,  $\beta = 92.99(3)^\circ$ ,  $V = 2801.8(10)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.633$  g cm<sup>-3</sup>,  $\mu = 0.450$  mm<sup>-1</sup>,  $T = 301$  K,  $2\theta_{\text{max}} = 51.26^\circ$ , GOF = 1.084,  $R_1 = 0.0364$ ,  $wR_2 = 0.096$ . Crystal data for **2a**· $2\text{C}_5\text{H}_{12}$ : triclinic,  $P\bar{1}$ ,  $a = 11.194(2)$  Å,  $b = 11.597(2)$  Å,  $c = 14.722(3)$  Å,  $\alpha = 78.01(3)^\circ$ ,  $\beta = 78.97(3)^\circ$ ,  $\gamma = 72.70(3)^\circ$ ,  $V = 1767.6(6)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.171$  g cm<sup>-3</sup>,  $\mu = 0.311$  mm<sup>-1</sup>,  $T = 301$  K,  $2\theta_{\text{max}} = 50.98^\circ$ , GOF = 1.045,  $R_1 = 0.0403$ ,  $wR_2 = 0.117$ .