# **ORGANOMETALLICS**

# Cis—Trans Ring Substituent Isomerism in Cyano-Substituted Metallathietane-3,3-dioxide Complexes of Platinum(II) and Palladium(II)

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**ABSTRACT:** Reactions of the platinum complexes *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], [PtCl<sub>2</sub>(dppf)], or [PtCl<sub>2</sub>(dppe)], and the palladium complexes, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] or [PdCl<sub>2</sub>(dppe)], with bis(cyanomethyl)sulfone NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN in methanol with added trimethylamine base gave the new cyano-substituted metallathietane-3,3dioxide complexes [M{CH(CN)SO<sub>2</sub>CH(CN)}L<sub>2</sub>] (M = Pd, Pt) in good yields and purities. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy indicates that (in the majority of cases) the products are formed as a mixture of cis and trans isomers, with regard to the disposition of the cyano groups across the four-membered ring. An X-ray structure determination on a crystal of [Pd{CH(CN)SO<sub>2</sub>CH(CN)}(PPh<sub>3</sub>)<sub>2</sub>] showed it to be of the cis isomer, the first structurally characterized cis isomer of this type of complex. The four-membered palladacyclic ring is highly planar, in contrast to other



metallathietane-3,3-dioxide complexes that have puckered rings. Factors influencing the relative abundances of the two isomers of  $[Pd{CH(CN)SO_2CH(CN)}(PR_3)_2]$  have been investigated by means of NMR spectroscopy and DFT calculations.

# INTRODUCTION

Small-ring metallacyclic complexes are of fundamental interest for their structural properties and reactivity, with the best-known examples of such ring systems being metallacyclobutanes.<sup>1,2</sup> The metallathietane-3,3-dioxide ring system, M-CHR-SO<sub>2</sub>-CHR, is known for a relatively small number of transition metals, specifically, platinum(II), palladium(II), nickel(II), and gold-(III). A series of platinum(II), palladium(II), and nickel(II) complexes [M(PhCHSO<sub>2</sub>CHPh)L<sub>2</sub>] 1 were synthesized from the parent chloride complexes [MCl<sub>2</sub>L<sub>2</sub>] by reaction with the dianion [PhCHSO<sub>2</sub>CHPh]<sup>2-3</sup> Complexes [M{CH(COPh)- $SO_2CH(COPh)$  [L<sub>2</sub>] 2 (with electron-withdrawing COPh substituents on the ring carbon) have been prepared for platinum(II) and palladium(II) using a convenient method employing silver(I) oxide as a mild base and halide-abstracting agent,<sup>4</sup> while gold(III) analogues have been prepared using Ag<sub>2</sub>O in dichloromethane<sup>5</sup> or Me<sub>3</sub>N in refluxing methanol.<sup>6</sup> The nature of the ring substituent plays a significant role in the chemistry of the resulting metallacyclic complex. This is exemplified by the observation that platinathietane-3,3-dioxide complexes 1 with phenyl ring substituents undergo ligand substitution reactions with <sup>t</sup>BuNC, but when more strongly electron-withdrawing COPh substituents are present, ligand substitution and insertion reactions both occur, giving ring-expanded products.<sup>6,7</sup>

Metallathietane-3,3-dioxide ring systems are typically slightly puckered; this has been the subject of a theoretical study, which found a very low energy barrier to inversion of the fourmembered M-C-S-C ring.<sup>8</sup> In all four crystallographically characterized metallathietane-3,3-dioxide complexes to date (vide infra), the two R substituents have been found to have a trans arrangement on the four-membered ring, which is corroborated by the observation of a single isomer in NMR spectroscopic studies. However, in one case involving cycloaurated gold(III) complexes, one isolated product derived from  $(PhC(O)CH_2)_2SO_2$  showed additional signals attributable to the cis isomer.<sup>6</sup>

In this contribution, we report the synthesis of new metallathietane-3,3-dioxide complexes of platinum(II) and palladium(II) containing cyano substituents derived from NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN, together with an experimental and theoretical investigation of the occurrence of cis and trans isomers for these complexes. The only previously reported metallathietane-3,3-dioxide complexes derived from this sulfone are a series of cycloaurated gold(III) complexes, which were too insoluble for NMR characterization, and it is unknown if they exist as cis/trans isomers.<sup>6</sup>

## RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization. The platinum(II) and palladium(II) starting complexes  $[MCl_2L_2]$  used in this study were conveniently prepared by ligand

Received: November 17, 2011 Published: June 28, 2012 substitution of the *cyclo*-octa-1,5-diene (cod) ligand of  $[MCl_2(cod)]$  (M = Pd, Pt) with 2 mol equiv of a monodentate phosphine (PPh<sub>3</sub>) or 1 mol equiv of a bis-phosphine [1,2-bis(diphenylphosphino)ethane (dppe) or 1,1'-bis-(diphenylphosphino)ferrocene (dppf)]. The  $[MCl_2L_2]$  complexes could be either isolated or generated in situ. Reaction of  $[MCl_2L_2]$  with 1 mol equiv of bis(cyanomethyl)sulfone  $[NCCH_2SO_2CH_2CN]$  and excess trimethylamine in refluxing methanol for 30 min, followed by addition of water, gave good yields of the new cyano-substituted platina- and pallada-thietane-3,3-dioxide complexes **3a-3e**, Scheme 1. The complexes are



white or cream-colored, with the obvious exception of the ferrocene-derived complex **3b**, which is yellow. The complexes are (surprisingly) poorly soluble in most organic solvents, with only limited solubility in chlorinated hydrocarbon solvents (CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>) in which other platina- and pallada-thietane-3,3-dioxide complexes show good solubility. Cycloau-rated gold(III) complexes of this ligand have also been found to have low solubility.<sup>6</sup> The complexes were characterized by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, mass spectrometry, IR spectroscopy, and elemental analysis.

The 2,2-bipyridine (bipy) complex **3f** was similarly prepared by reaction of  $[PdCl_2(bipy)]$  with NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN and Me<sub>3</sub>N and was isolated as a cream solid that was very insoluble in methanol and chlorinated solvents, such that it has not been possible to obtain satisfactory mass spectra (ESI or MALDI) for this complex. Evidence for the formation of this complex was based on satisfactory microanalytical data.

The IR spectra of complexes 3a-3e showed a medium intensity sharp absorption due to the cyano groups in the range of 2213–2218 cm<sup>-1</sup> for the platinum complexes 3a-3c, and slightly lower, around 2202 cm<sup>-1</sup>, for the palladium complexes 3d and 3e. The symmetric and asymmetric SO<sub>2</sub> stretches appear around 1310 and 1125 cm<sup>-1</sup>. In comparison, the parent sulfone NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN shows a higher CN stretching frequency at 2267 cm<sup>-1</sup> (similar to the range for alkyl nitriles, which fall in the range of 2240–2260 cm<sup>-1</sup>) and higher SO<sub>2</sub> stretches at 1338 and 1149 cm<sup>-1</sup>.

Positive-ion ESI mass spectrometry was used to characterize the complexes. However, reproducibility was rather low, and the observed ions were dependent on the instrument and conditions used. The best spectra were obtained when ammonium formate was added as an ionization aid, producing  $[M + NH_4]^+$  and  $[2M + NH_4]^+$  ions as the dominant ions at low cone voltages. Increasing fragmentation conditions produced  $[M + H]^+$ . The intensity of the  $[2M + NH_4]^+$  ions decreased, but fragmentation to  $[2M + H]^+$  was not significant, indicating that the ammonium cation is instrumental in the aggregation of the dimeric species. The platinum triphenylphosphine complex **3a** showed the fragment ion  $[Pt(C_6H_4PPh_2)(PPh_3)]^+$  (m/z 718) at cone voltages > 50 V, this ion being a typical fragment ion observed for Pt–PPh<sub>3</sub> complexes.<sup>9–11</sup>



**Figure 1.** Part of the <sup>1</sup>H NMR spectrum of [Pt{CH(CN)SO<sub>2</sub>CH(CN)}(dppf)] **3b** showing the Pt–CH resonances of the cis ( $\delta$  3.07) and trans ( $\delta$  2.87) isomers of this complex. The inset shows the <sup>1</sup>H NMR resonance of the CH protons of the complex *trans*-[Pt{CH(COPh)SO<sub>2</sub>CH(COPh)}(PPh<sub>3</sub>)<sub>2</sub>] **2a**.

An NMR spectroscopic study on the cyano-substituted metallathietane-3,3-dioxide complexes reveals the presence of cis and trans isomers. For example, the  ${}^{31}P{}^{1}H$  NMR spectrum of 3a shows major and minor singlet resonances assigned to the trans and cis isomers at  $\delta$  13.5 and 13.4, respectively, showing very similar couplings to <sup>195</sup>Pt of 2844 and 2854 Hz. The <sup>1</sup>H NMR spectrum of a sample of [Pt{CH(CN)SO<sub>2</sub>CH(CN)}-(dppf)] 3b is shown in Figure 1 and clearly shows the Pt-CH resonances due to the cis and trans isomers at ca.  $\delta$  3.07 and 2.87, respectively. These are substantially shielded compared with the CH<sub>2</sub> protons in NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN ( $\delta$  4.33). The trans isomer is readily identified as the major species, by comparison of its distinctive resonance (a second-order doublet with satellites due to <sup>195</sup>Pt coupling) with those of [Pt{CH(COPh)SO<sub>2</sub>CH-(COPh) (PPh<sub>3</sub>)<sub>2</sub> **2a**, which has been crystallographically characterized as the trans isomer and found to be isomerically pure by NMR spectroscopy (see Figure 1, inset).<sup>4</sup> The PtCH protons of the cis isomer of 3b appear also as a doublet, partly overlapping the <sup>195</sup>Pt satellite resonances due to the trans isomer. The cyano-substituted complexes all give similar <sup>1</sup>H spectroscopic features for the CH protons of the cis and trans isomers.

Different reaction conditions have been employed to investigate potential changes in the isomer ratios. The reaction between cis-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN was carried out in dichloromethane solution with Ag<sub>2</sub>O as the base (conditions that have been previously used to prepare metallacyclic complexes, including metallathietane-3,3-dioxides<sup>4</sup>); the product is easily isolated by precipitation with petroleum spirits. When the reaction is carried out at room temperature for 1 h using Ag<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>, the isolated product contained mainly the cis isomer, but longer reaction times gave more trans isomer. Likewise, a shorter reflux time (10 min) using Me<sub>3</sub>N in MeOH gave roughly equal amounts of cis and trans isomers. These observations suggested that the cis isomer may be the kinetically favored product and that a theoretical study to investigate the relative stabilities of the cis and trans isomers was warranted (vide infra).

X-ray Crystal Structure Determination. To date, there have only been four structure determinations on metallathietane-3,3-dioxide complexes, these being  $[Pt(CHPhSO_2CHPh)-(AsPh_3)_2]$  1a,<sup>3</sup>  $[Pt{CH(COPh)SO_2CH(COPh)}(PPh_3)_2]$  2a,<sup>4</sup>  $[Pd{CH(COPh)SO_2CH(COPh)}(PMePh_2)_2]$  2b,<sup>4</sup> and  $[(MeOC_6H_3CH_2NMe_2)Au{CH(COPh)SO_2CH(COPh)}]$  4.<sup>5</sup> Therefore, an X-ray structure was determined on a cyanosubstituted complex in order to investigate its structural features. Suitable crystals of the triphenylphosphine-palladium complex 3d were obtained from dichloromethane-diethyl ether.

The molecular structure of the core of the complex is shown in Figure 2, together with the atom numbering scheme, while selected bond lengths and angles are given in Table 1. The structure confirms the complex as a cis cyano-substituted palladathietane-3,3-dioxide ring system; this is the first structurally characterized example of a cis-disubstituted metallathietane ring system, all previous examples being the trans isomers.

The four-membered palladacycle is almost planar, with only a  $1.05(12)^{\circ}$  angle between the C(1)–S(1)–C(3) and C(1)–Pd–C(3) planes. However, there is a significant distortion of the palladium(II) center from the idealized square-planar geometry, with an angle of 19.09(7)° between the P–Pd–P and C–Pd–C planes. The distortion from square-planar geometry is conveniently quantified by the  $\tau_4$  parameter of Houser and coworkers,<sup>12</sup> which gives a value of 0.258 for 3d [compared to



Figure 2. Molecular structure of the core of the cis isomer of  $[Pd{CH(CN)SO_2CH(CN)}(PPh_3)_2]$  3d showing the atom numbering scheme. Only *ipso*-C of the phenyl rings are shown, and H atoms are omitted.

theoretical  $\tau_4$  values of 0 and 1 for a perfect square plane and tetrahedron, respectively]. This contrasts with the only other structure of a palladathietane-3,3-dioxide complex 2b, where the four-membered ring is considerably more puckered [dihedral angle between the C-Pd-C and C-S-C planes of  $30.2(2)^{\circ}$ ], but the tetrahedral distortion of the palladium(II) center is relatively small, with a dihedral angle of  $19.09(7)^{\circ}$  between the P–Pd–P and C–Pd–C planes, and a  $\tau_4$  parameter of 0.167. The bulky C(O)Ph substituents in the trans isomer **2b** adopt pseudoaxial and pseudo-equatorial positions on the puckered fourmembered ring, in order to minimize steric interactions with the PMePh<sub>2</sub> ligands. The cyano groups of **3d** have less steric bulk and are presumably easily accommodated in either the cis or the trans isomers. The planar four-membered ring in 3d results in eclipsing of the S(1)-O(2) bond with the two C–CN bonds, C(1)-C(2)and C(3)-C(4), such that the O(2)-S(1)-C(1)-C(2) and O(2)-S(1)-C(3)-C(4) torsion angles are 11.4(3)° and 8.0(3) °, respectively.

The Pd–C distances of **3d** [2.119(3) and 2.130(3) Å] are similar to the Pd–C bond distances in **2b** [2.148(6) and 2.122(6) Å].<sup>4</sup> The bite angle of the NCCHSO<sub>2</sub>CHCN ligand at palladium is 75.77(11)°, which also compares favorably with **2b** [74.7(2)°]. Likewise, the C–S–C bond angle at the sulfone group of **3d** is 95.49(13)°, similar to that of **2b** [95.9(3)°]. However, the S–C–Pd bond angles in **3d** [93.92(13)° and 94.81(13)°] are notably larger than those in **2b** [91.1(2)° and 90.0(2)°],<sup>4</sup> consistent with the lack of puckering in the cyanosubstituted ring.

The Pd–P bond distances of 3d [Pd–P(1) 2.3225(7) and Pd-P(2) 2.3307(8) Å are longer than those of **2b** [2.311(2) and 2.295(2) Å];<sup>4</sup> however, the phosphine ligands are different  $[PPh_3 \text{ in } 3d \text{ versus } PMePh_2 \text{ in } 2b]$ . A comparison of the X-ray structures of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (CSD refcode: BISROK)<sup>13</sup> and the monoclinic form of cis-[PtCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>] (CSD refcode: BAZKUI01)<sup>14</sup> shows that the Pt-P bonds in the PMePh<sub>2</sub> complex are also slightly shorter [2.2458(1) and 2.2445(1) Å] compared to the PPh<sub>3</sub> complex [2.2647(4) and 2.2507(4) Å], so it is not possible to obtain information on trans influences of the C donor ligands based on structural data alone. However, from <sup>31</sup>P NMR data, the value of  ${}^{1}J(PtP)$  for the trans isomer of **3a** (2844 Hz) is slightly larger than that of the corresponding triphenylphosphine complex [Pt{CH(COPh)SO<sub>2</sub>CH(COPh)}-(PPh<sub>3</sub>)<sub>2</sub>]<sup>2</sup>a (2817 Hz),<sup>4</sup> indicating that the CH(CN) group has a slightly smaller trans influence.<sup>15</sup>

Table 1. Selected Bond Lengths (Å) and Angles (deg) for	· [Pd{CH(CN)SO2CH(CN)}(PPh3)2] 3d with Standard Uncertainty
Values in Parentheses	

Pd-C(1)	2,130(3)	Pd-C(3)	2 119(3)
Pd-P(1)	2.130(3)	Pd-P(2)	2.3307(8)
S(1) = O(2)	1.442(3)	S(1) = O(1)	1.443(3)
S(1) - C(3)	1.754(3)	S(1) - C(1)	1.771(3)
C(1) - C(2)	1.430(4)	C(2) - N(1)	1.155(4)
C(3) - C(4)	1.418(5)	C(4) - N(2)	1.148(5)
C(1) - Pd - C(3)	75.77(11)	C(3) - Pd - P(1)	92.77(8)
C(1) - Pd - P(2)	93.16(8)	P(1)-Pd-P(2)	101.11(3)
O(1)-S(1)-O(2)	119.15(17)	O(2)-S(1)-C(3)	111.73(15)
O(1)-S(1)-C(3)	107.83(15)	O(2)-S(1)-C(1)	110.53(15)
O(1)-S(1)-C(1)	109.51(16)	C(1)-S(1)-C(3)	95.49(13)
C(2)-C(1)-S(1)	114.4(2)	C(2)-C(1)-Pd	122.0(2)
S(1)-C(1)-Pd	93.92(13)	N(1)-C(2)-C(1)	179.2(3)
C(4)-C(3)-S(1)	115.6(2)	C(4) - C(3) - Pd	103.5(2)
S(1)-C(3)-Pd	94.81(13)	N(2)-C(4)-C(3)	176.5(4)



**Figure 3.** A view in projection down the *a* axis of the unit cell contents for the cis isomer of  $[Pd{CH(CN)SO_2CH(CN)}(PPh_3)_2]$  3d. Molecules assemble into supramolecular layers in the *ac* plane via C-H···O (orange dashed lines), C-H···N (blue), and C-H··· $\pi$  (not shown) interactions. Layers are connected along the *b* axis via C-H··· $\pi$  (purple dashed lines).

The crystal structure of **3d** is stabilized by a combination of C– H···O, C–H···N,  $\pi$ ··· $\pi$ , and C–H··· $\pi$  interactions (refer to the Experimental Section). The C–H···O and C–H···N contacts serve to link molecules into a supramolecular array in the *ac* plane; additional stabilization to the layers is afforded by C– H··· $\pi$  interactions. Phenyl rings lie to either side of the layers and interdigitate with adjacent layers along the *b* direction, allowing for the formation of  $C-H\cdots\pi$  interactions. A view of the unit cell contents for **3d** is given in Figure 3.

**Theoretical Study.** The molecular structure of both cis and trans conformers of complex 3d, namely, *cis*- $[Pd{CH(CN)-SO_2CH(CN)}(PPh_3)_2]$  3tc and *trans*- $[Pd{CH(CN)SO_2CH-CH(CN)}(Ph_3)_2]$  3tc and *trans*- $[Pd{CH(CN)}(Ph_3)_2]$  3tc a

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Figure 4. Optimized geometries of the cis and trans conformers of the actual complex  $[Pd{CH(CN)SO_2CH(CN)}(PPh_3)_2]$ , 3tc and 3tt, and the model complex  $[Pd{CH(CN)SO_2CH(CN)}(PH_3)_2]$ , 3tc and 3ttm.

(CN) (PPh<sub>3</sub>)<sub>2</sub>] **3tt**, have been optimized at the density functional level of theory using the B3LYP functional. Both conformers are minima in the potential surface of the molecule, as the calculation of the Hessian gave no imaginary frequencies. Figure 4 shows the optimized structures adopting the  $C_1$ symmetry point group with an essentially planar [PdCSC] metallathietane ring. Selected calculated bond lengths and angles are given in Table 2; experimental bond lengths determined by X-ray structure analysis for the cis complex **3d** are also given for comparison. An overall agreement has been found between the calculated and experimental structures of the cis complex. The Pd–P bond lengths are longer than the experimental values. This lengthening could be attributed to the fact that, according to previous theoretical studies, the lengths of metal–ligand bonds tend to become shorter in the solid state because of interatomic interactions.<sup>16,17</sup> The differences between calculated and experimental bond angles are not very large and need not be further discussed. According to the calculation in the gas phase,

Table 2. Selected Calculated Bond Lengths (Å) and Angles (deg) for Cis and Trans Conformers of the Actual Complex  $[Pd{CH(CN)SO_2CH(CN)}(PPh_3)_2]$ , 3tc and 3tt, and the Model Complex  $[Pd{CH(CN)SO_2CH(CN)}(PH_3)_2]$ , 3tcm and 3ttm<sup>*a*,*b*</sup>

	3tc	3tcm	exptl <sup>c</sup>	3tt	3ttm
Pd-P(1)	2.380	2.395	2.330	2.383	2.396
Pd-P(2)	2.367	2.395	2.322	2.356	2.396
Pd-C(1)	2.128	2.121	2.119	2.147	2.118
Pd-C(2)	2.154	2.121	2.130	2.145	2.118
S(1) - O(1)	1.475	1.467	1.442	1.468	1.465
S(1) - O(2)	1.466	1.464	1.441	1.471	1.465
S(1) - C(1)	1.808	1.820	1.754	1.816	1.820
S(1) - C(3)	1.812	1.820	1.771	1.808	1.820
C(1) - C(2)	1.435	1.434	1.418	1.432	1.434
C(3) - C(4)	1.433	1.434	1.430	1.434	1.434
C(1) - H(1)	1.090	1.092		1.090	1.092
C(3) - H(2)	1.090	1.092		1.089	1.092
C(2) - N(1)	1.166	1.165	1.147	1.166	1.165
C(4) - N(2)	1.165	1.165	1.151	1.166	1.165
C(1)-Pd-C(3)	74.8	75.5	75.8	74.4	76.0
C(1)-Pd-P(2)	92.3	92.5	92.8	93.8	76.0
C(3)-Pd-P(1)	92.3	92.5	93.1	92.7	92.3
P(1)-Pd-P(2)	101.0	99.4	101.1	101.9	99.7
C(2) - C(1) - Pd	107.9	112.3	103.5	112.0	111.8
C(4)-C(3)-Pd	116.0	112.3	122.0	107.4	111.8
S(1)-C(1)-Pd	94.4	95.8	94.8	94.7	96.2
S(1)-C(3)-Pd	93.4	95.8	93.9	94.9	96.2
O(1) - S(1) - O(2)	120.5	121.7	119.2	120.6	121.8
O(1) - S(1) - C(1)	106.4	109.2	107.8	111.0	108.8
O(2) - S(1) - C(1)	113.5	110.7	111.8	109.8	110.9
O(1) - S(1) - C(3)	107.0	109.2	109.5	112.9	110.9
O(2) - S(1) - C(3)	113.6	110.7	110.5	107.1	108.8
C(2)-C(1)-S(1)	115.9	116.6	115.6	113.2	117.0
C(4) - C(3) - S(1)	115.5	116.6	114.4	113.8	117.0
N(1)-C(2)-C(1)	176.8	175.5	176.5	178.0	175.7
N(2)-C(4)-C(3)	177.9	175.5	179.2	177.2	175.7
Numbering scheme as in Figure 4 <sup>b</sup> Phonyl hydrogens not shown for					

"Numbering scheme as in Figure 4. "Phenyl hydrogens not shown tor clarity. "Experimental data for complex 3d.

the two conformers have actually the same energy. The trans isomer is found to be the global minimum, whereas the cis isomer, being experimentally isolated, has been found to be only 0.1 kcal/mol higher in energy.

To explore a possible effect of the steric hindrance of the bulky phosphine ligands to the cis-trans energy difference, the molecular structure of both cis and trans conformers of a model complex, where the PPh<sub>3</sub> phosphine ligands have been replaced by PH<sub>3</sub>, namely, *cis*-[Pd{CH(CN)SO<sub>2</sub>CH(CN)}-(PH<sub>3</sub>)<sub>2</sub>] **3tcm** and *trans*-[Pd{CH(CN)SO<sub>2</sub>CH(CN)}(PH<sub>3</sub>)<sub>2</sub>] complex **3ttm**, has been optimized at the same level of theory. Although the optimizations had no symmetry constraints, the cis conformer adopts a planar  $C_s$  geometry. The actual symmetry of the calculated trans conformer is  $C_2$  with a small deviation from planarity, with the angle between the [PdCSC] metallathietane ring and the [PPdP] plane being equal to 3.9°. The cis-trans energy difference is very small and in the case of the model complex 0.4 kcal/mol in favor of the trans isomer.

As the dipole moment of the cis isomer, **3tcm**, in the gas phase (12.2 D) was predicted to be a little larger than that of the trans isomer **3ttm** (11.4 D), one expects that a polar solvent, such as methanol, would stabilize the cis isomer. After a full

reoptimization of the model complexes **3tcm** and **3ttm** in the presence of the methanol solvent starting from the geometries calculated in the gas phase, the energy difference has been found to be equal to 0.2 kcal/mol with the trans conformer being again more stable. The energy difference in the presence of dichloromethane has been calculated to be equal to that found in the gas state (0.4 D). Thus, the isolation of the cis or trans isomer could be attributed to small differences in the reaction and precipitation conditions. Finally, there are no major differences between the gas-phase structures and those calculated in the presence of the solvents. The largest deviation of bond distances is about 0.02 Å, while that of bond angles is about  $2^{\circ}$ .

#### CONCLUSIONS

A series of new platinum(II) and palladium(II) metallathietane-3,3-dioxide complexes bearing cyano ring substituents have been synthesized for the first time and shown by NMR spectroscopy to consist of a mixture of cis and trans isomers, with the first crystal structure of a cis isomer of such metallacycles being reported. The energies of the cis and trans isomers were found to be very similar in this system.

### EXPERIMENTAL SECTION

**General.** <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded at 300.13 and 121.5 MHz, respectively, on a Bruker AC300P spectrometer in CDCl<sub>3</sub>, unless otherwise stated. Elemental analyses were obtained by the Campbell Microanalytical Laboratory at the University of Otago, Dunedin, New Zealand. Infrared spectra were recorded as KBr disks on a PerkinElmer Spectrum 100 FT-IR spectrophotometer. Melting points were determined on a Reichert-Jung hot-stage apparatus and are uncorrected.

ESI mass spectra were recorded on a (low-resolution) VG Platform II instrument, or on a (high-resolution) Bruker MicrOTOF instrument, the latter calibrated using aqueous sodium formate solution. Samples (dissolved in a small quantity of dichloromethane) were diluted (to ca.  $0.1 \text{ mg mL}^{-1}$ ) with methanol and centrifuged prior to analysis. In some cases, a drop of dilute aqueous NaCl or NH<sub>4</sub>[HCO<sub>2</sub>] was added as an ionization aid. Ion identification was facilitated by comparison of observed and calculated isotope distribution patterns, the latter obtained from the Isotope program, <sup>18</sup> or from proprietary instrument-based software.

The complexes  $[PtCl_2(cod)]$ ,<sup>19</sup>  $[PdCl_2(cod)]$ ,<sup>20</sup> and  $[PdCl_2(bipy)]^{21}$  were prepared by the literature procedures. The complexes  $[PtCl_2L_2]$  were generated by addition of 2 mol equiv of L to a stirred suspension of  $[PtCl_2(cod)]$  in methanol, followed by stirring for 10 min.<sup>22</sup> The palladium analogues were prepared in the same way from  $[PdCl_2(cod)]$  and the phosphine in dichloromethane, followed by precipitation with petroleum spirits. NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN was obtained from Lancaster Synthesis, or was prepared by the literature procedure,<sup>23</sup> and PhC(O)CH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>C(O)Ph was prepared as described previously.<sup>4</sup> Aqueous trimethylamine solution (30%) was used as supplied by BDH. PPh<sub>3</sub> (BDH) was used as supplied, whereas dppe<sup>24</sup> and dppf<sup>25</sup> were prepared by the literature procedures. All reactions were carried out in laboratory reagent grade methanol without further purification or attempts to exclude air or moisture.

Synthesis of  $[Pt{CH(COPh)SO_2CH(COPh)}{PPh_3}]$  2a. The complex has been previously synthesized from *cis*- $[PtCl_2(PPh_3)_2]$  and PhC(O)CH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>C(O)Ph using Ag<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub>.<sup>4</sup> A suspension of *cis*- $[PtCl_2(PPh_3)_2]$  (356 mg, 0.462 mmol) and PhC(O)CH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>C-(O)Ph (142 mg, 0.470 mmol) in methanol (30 mL) with trimethylamine (1 mL) was refluxed with stirring for 3 h to give a white suspension in a cream solution. After cooling to room temperature, the product was filtered, washed with cold methanol (5 mL), and dried under vacuum to give the product 2a as a white solid (318 mg, 69%) that was identified by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy as the pure trans isomer.

Synthesis of  $[M{CH(CN)SO_2CH(CN)}L_2]$  – General Method. To a stirred mixture of  $[MCl_2L_2]$  (either preformed or generated in situ) and 1 mol equiv of  $NCCH_2SO_2CH_2CN$  in methanol (30 mL) was added aqueous trimethylamine solution (1 mL, excess), and the mixture was refluxed for 30 min. Water (50 mL) was added, and the product was isolated by filtration, washed with cold water (10 mL) and diethyl ether (10 mL), and dried under vacuum.

**Synthesis of [Pt{CH(CN)SO<sub>2</sub>CH(CN)}(PPh<sub>3</sub>)<sub>2</sub>] 3a.** [PtCl<sub>2</sub>(cod)] (200 mg, 0.535 mmol) with triphenylphosphine (287 mg, 1.10 mmol) and NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN (77 mg, 0.535 mmol) gave **3a** (398 mg, 86%) as a white solid. mp 285–286 °C. Found: C, 56.0; H, 3.6; N, 3.4. C<sub>40</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>PtS ( $M_r$  861.25) requires C, 55.8; H, 3.7; N, 3.3%. Highresolution ESI MS: [M + H]<sup>+</sup> (m/z 862.184, calculated 862.138), [M + Na]<sup>+</sup> (m/z 884.166, calculated 884.120). Low-resolution ESI MS: [M + NH<sub>4</sub>]<sup>+</sup> (m/z 879, 100%), [2M + NH<sub>4</sub>]<sup>+</sup> (m/z 1741, 70%). MALDI-TOF MS: [M + H]<sup>+</sup> (m/z 862), [M + Na]<sup>+</sup> (m/z 884). IR  $\nu$ (CN): 2218 (m) cm<sup>-1</sup>,  $\nu$ (SO<sub>2</sub>) 1312 (vs) and 1129 (vs) cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR: trans isomer (major),  $\delta$  13.5 [s, <sup>1</sup>J(PtP) 2844]; cis isomer (minor),  $\delta$  13.4 [<sup>1</sup>J(PtP) 2854]. <sup>1</sup>H NMR:  $\delta$  7.65–7.28 (m, PPh<sub>3</sub>) cis isomer 3.14 [d, br, J(PH) 4.9, <sup>2</sup>J(PtH) 76] and trans isomer 3.06 [d, br, J(PH) 0.9, <sup>2</sup>J(PtH) 77].

**Synthesis of [Pt{CH(CN)SO<sub>2</sub>CH(CN)}(dppf)] 3b.** [PtCl<sub>2</sub>(cod)] (103 mg, 0.275 mmol) with dppf (153 mg, 0.276 mmol) and NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN (40 mg, 0.278 mmol) gave **3b** as a yellow solid (184 mg, 75%). Found: C, 50.2; H, 3.3; N, 3.1. C<sub>38</sub>H<sub>30</sub>N<sub>2</sub>FeO<sub>2</sub>P<sub>2</sub>PtS ( $M_r$ 891.58) requires C, 51.2; H, 3.4; N, 3.1%. MALDI TOF MS: [M + H]<sup>+</sup> (m/z 892), [M + Na]<sup>+</sup> (m/z 914). High-resolution ESI MS: [M + H]<sup>+</sup> (m/z 892.101, calculated 892.058), [M + Na]<sup>+</sup> (m/z 914.084, calculated 914.040). Low-resolution ESI MS: [M + NH<sub>4</sub>]<sup>+</sup> (m/z 909, 100%), [2M + NH<sub>4</sub>]<sup>+</sup> (m/z 1801, 30%). IR ν(CN): 2218 (m) cm<sup>-1</sup>, ν(SO<sub>2</sub>) 1311 (vs) and 1126 (vs) cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR: trans isomer (major), δ 13.9 [s, <sup>1</sup>J(PtP) 2912]; cis isomer (minor), δ 13.8 [<sup>1</sup>J(PtP) ca. 2940]. Selected <sup>1</sup>H NMR data: trans isomer (major) δ 2.87 [d, J(PH) 1.2, <sup>2</sup>J(PtH) 77]; cis isomer (minor), δ 3.07 [d, <sup>3</sup>J(PH) 4.9, <sup>2</sup>J(PtH) 78].

**Synthesis of [Pt{CH(CN)SO<sub>2</sub>CH(CN)}(dppe)] 3c.** [PtCl<sub>2</sub>(dppe)] (130 mg, 0.196 mmol) with NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN (29 mg, 0.201 mmol) gave **3c** (86 mg, 60%) as a white powder. Found: C, 48.3; H, 3.4; N, 3.8.  $C_{30}H_{26}N_2O_2P_2PtS$  ( $M_r$  735.61) requires C, 49.0; H, 3.6; N, 3.8%. High-resolution ESI MS: [M + H]<sup>+</sup> (m/z 736.128, calculated 736.091), [M + Na]<sup>+</sup> (m/z 758.111, calculated 758.073). Low-resolution ESI MS: [M + NH<sub>4</sub>]<sup>+</sup> (m/z 753, 100%), [2M + NH<sub>4</sub>]<sup>+</sup> (m/z 1488, 15%). IR  $\nu$ (CN): 2213 (m) cm<sup>-1</sup>,  $\nu$ (SO<sub>2</sub>) 1312 (vs) and 1124 (vs) cm<sup>-1</sup>.

**Synthesis of [Pd{CH(CN)SO<sub>2</sub>CH(CN)}(PPh<sub>3</sub>)<sub>2</sub>] 3d.** [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (200 mg, 0.285 mmol) with NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN (42 mg, 0.292 mmol) gave **3d** (183 mg, 83%) as a white powder. Found: C, 62.1; H, 4.1; N, 3.6.  $C_{40}H_{32}N_2O_2P_2PdS$  ( $M_r$  773.14) requires C, 62.1; H, 4.2; N, 3.6%. High-resolution ESI MS: [M + H]<sup>+</sup> (m/z 773.117, calculated 773.078), [M + Na]<sup>+</sup> (m/z 795.102, calculated 795.060). Low-resolution ESI MS: [M + NH<sub>4</sub>]<sup>+</sup> (m/z 790, 100%), [2M + NH<sub>4</sub> – PPh<sub>3</sub>]<sup>+</sup> (m/z 1302, 10%), [2M + NH<sub>4</sub>]<sup>+</sup> (m/z 1564, 55%). IR  $\nu$ (CN): 2203 (m) cm<sup>-1</sup>,  $\nu$ (SO<sub>2</sub>) 1310 (vs) and 1124 (vs) cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR: trans isomer (major),  $\delta$  25.6 (s); cis isomer (minor),  $\delta$  25.4 (s). Selected <sup>1</sup>H NMR data: trans isomer (major)  $\delta$  2.70 (m); cis isomer (minor),  $\delta$  2.78 [d, <sup>3</sup>I(PH) 3.1].

**Synthesis of [Pd{CH(CN)SO<sub>2</sub>CH(CN)}(dppe)] 3e.** [PdCl<sub>2</sub>(dppe)] (255 mg, 0.443 mmol) with NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN (64 mg, 0.444 mmol) gave **3e** as a white solid (266 mg, 93%). Found: C, 55.4; H, 4.1; H, 4.3. C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>PdS ( $M_r$  646.98) requires C, 55.7; H, 4.1; N, 4.3%. MALDI-TOF MS: [M + H]<sup>+</sup> (m/z 647), [M + Na]<sup>+</sup> (m/z 669). High-resolution ESI MS: [M + H]<sup>+</sup> (m/z 647.061, calculated 647.031), [M + Na]<sup>+</sup> (m/z 669.045, calculated 669.013). Low-resolution ESI MS: [M + NH<sub>4</sub>]<sup>+</sup> (m/z 664, 100%), [2M + NH<sub>4</sub>]<sup>+</sup> (m/z 1312, 30%). IR ν(CN): 2202 (m) cm<sup>-1</sup>, ν(SO<sub>2</sub>) 1309 (vs) and 1121 (vs) cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR: trans isomer (major), δ 50.7 (s); cis isomer (minor), δ 51.2 (s). Selected <sup>1</sup>H NMR data: 2.67–2.31 (m, CH<sub>2</sub> of dppe); trans isomer (major) δ 3.01 [d, br, *J*(PH) 3.7]; cis isomer (minor), δ 3.16 [d, *J*(PH) 5.2].

**Synthesis of [Pd{CH(CN)SO<sub>2</sub>CH(CN)}(bipy)] 3f.** [PdCl<sub>2</sub>(bipy)] (158 mg, 0.474 mmol) with NCCH<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>CN (69 mg, 0.479 mmol) gave **3f** as a cream solid (155 mg, 81%). Found: C, 41.0; H, 2.3; N, 13.4.

 $C_{14}H_{10}N_4O_2PdS$  ( $M_r$  404.75) requires C, 41.5; H, 2.5; N, 13.8%. The complex was too insoluble to record NMR or ESI mass spectra.

X-ray Crystal Structure Determination of [Pd{CH(CN)SO2CH-(CN)}(PPh<sub>3</sub>)<sub>2</sub>] 3d. Colorless crystals of 3d were grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex at room temperature. A crystal having dimensions of  $0.15 \times 0.25 \times 0.30$  mm was selected for the study. Data were collected at 103(2) K on a Rigaku AFC12/SATURN724 diffractometer using Mo K $\alpha$  radiation so that  $\theta_{max}$ =  $27.5^{\circ}$ . The data set was reduced using CrystalClear<sup>26</sup> and corrected for absorption effects.<sup>27</sup> The structure was solved by direct methods with SHELXS-97<sup>28</sup> and refinement (anisotropic displacement parameters, hydrogen atoms in the riding model approximation, and a weighting scheme of the form  $w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 2.594P]$  for  $P = (F_o^2 + 2F_c^2)/3)$  was on  $F^2$  by means of SHELXL-97.<sup>26</sup> The maximum residual electron density peak (1.71 e Å<sup>-3</sup>) was located in the vicinity of the S(1)atom and is consistent with an alternative site for the O(2) atom being 1.50 Å from S(1) and 1.21 Å from O(2). Despite the low temperature of the analysis, high thermal motion is also noted in some of the other positions, in particular, for the N(1) atom. This may indicate an alternate conformation for the four-membered ring, but none was discerned. Crystallographic data and final refinement details are given in Table 3. Figures 2 and 3 were drawn with DIAMOND,<sup>29</sup> using arbitrary spheres. Data manipulation and interpretation were with WinGX<sup>30</sup> and PLATON.31

#### Table 3. Crystallographic Details for 3d

formula	CHNOPPAS
	$C_{40} I_{32} I_{2} O_{2} r_{2} r_{0} S$
molecular wt	//3.08
T/K	103(2)
cryst syst	triclinic
space group	$P\overline{1}$
a (Å)	10.8099(18)
b (Å)	12.655(2)
c (Å)	13.609(2)
$\alpha$ (deg)	103.769(2)
$\beta$ (deg)	105.322(3)
γ (deg)	93.471(2)
$V(Å^3)$	1728.7(5)
Ζ	2
$D_{\text{calc}} (\text{g cm}^{-3})$	1.485
No. reflns meas.	13 737
No. unique reflns	7877
No. observed reflns $[I > 2\sigma(I)]$	7436
$R_1 \left[ I > 2\sigma(I) \right]$	0.041
$wR_2$ (all data)	0.095

Intermolecular Interactions in the Crystal Structure of **3d**. Interactions Leading to the Supramolecular Array. C(10)-H-(10)···O(1)<sup>i</sup> = 2.30 Å, C(10)···O(1)<sup>i</sup> = 3.206(4) Å, with angle at H(10) = 160°; C(31)-H(31)···N(1)<sup>ii</sup> = 2.57 Å, C(31)···N(1)<sup>ii</sup> = 3.444(5) Å, with angle at H(31) = 154°; C(33)-H(33)···N(2)<sup>iii</sup> = 2.41 Å, C(33)···N(2)<sup>iii</sup> = 3.277(5) Å, with angle at H(33) = 151°; C(3)-H(3)···Cg(C17-C22) = 2.81 Å, C(3)···Cg(C17-C22) = 3.653(3) Å, with angle at H(3) = 143°.

Interactions Linking the Supramolecular Layers. C(25)-H-(25)...Cg(C35-C40)<sup>iv</sup> = 2.50 Å, C(25)...Cg(C35-C40)<sup>iv</sup> = 3.389(3) Å, with angle at H(25) = 156°; C(13)-H(13)...Cg(C17-C22)<sup>v</sup> = 2.95 Å, C(13)...Cg(C17-C22)<sup>v</sup> = 3.842(3) Å, with angle at H(25) = 157°. Symmetry operations - *i*: 1 - x, 1 - y, 2 - z; *ii*: 1 - x, 1 - y, 1 - z; *iii*: 1 + x, y, z; *iv*: -x, -y, 1 - z; v: -x, -y, 2 - z.

**Computational Details.** For the DFT calculations, the hybrid B3LYP method was applied with Becke's three-parameter functional<sup>32</sup> and the nonlocal correlation provided by the LYP expression.<sup>33</sup> The geometries of all the studied complexes were fully optimized using analytical gradient techniques, and a frequency calculation after each geometry optimization ensured that the calculated structures are real minima or transition states in the potential energy surface of the

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molecules. Calculations have been carried out on the actual complexes and on model complexes where the bulky substituents of the phosphine ligands have been replaced with hydrogen atoms. For the Pd atom, we used the LANL2DZ small-core relativistic effective core potential of Hay and Wadt<sup>34</sup> and the "Basis set II" (BS II) of Frenking and co-workers,<sup>35</sup> which is that of Hay and Wadt contracted to [441/2111/31]. For the ligand atoms, we used the standard 6-31G(d,p),<sup>36–39</sup> except for the atoms of the phosphines' substituents, where no polarization functions were used. These basis sets have been used in our previous theoretical study of related four-membered palladacycles.<sup>8</sup> The calculations in the presence of solvent were carried out using the polarized continuum model (PCM) of Tomasi and co-workers<sup>40,41</sup> with acetone ( $\varepsilon = 20.7$ ) and dichloromethane ( $\varepsilon = 8.93$ ). All calculations were carried out using the Gaussian 03W, version 6.0, system of programs.<sup>42</sup>

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#### Notes

The authors declare no competing financial interest.

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