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# Stereoselective thiirane desulfurization controlled by a bridging or terminal acyl ligand: Concerted vs. S<sub>N</sub>2 pathways



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#### ABSTRACT

An acyl-bridged heterodinuclear Pt/Mn complex [(dppe)Pt( $\mu$ -C(O)Np-1 $\kappa$ C,2 $\kappa$ O)—Mn(CO)<sub>4</sub>] (Np = neopentyl, –CH<sub>2</sub>CMe<sub>3</sub>) has been prepared and unambiguously characterized. Upon reaction with thiiranes, this species is able to facilitate the direct desulfurization of three-membered S-heterocycles to produce olefins with complete retention of stereochemistry, with kinetic details supporting a concerted mechanism for thiirane desulfurization. Conversion of this species to a non-bridged, opened Pt/Mn complex [(dppe)(NpC(O))Pt –Mn(CO)<sub>5</sub>] can be effected by reaction with CO<sub>(g)</sub> in benzene solution. These non-bridged species display the opposite reactivity with thiiranes, generating the isomer with an inverted stereochemistry. Isolation of key thiamanganacyclic intermediates indicate that inversion occurs in the first C–S bond cleavage event, while the second desulfurization step proceeds with retention to produce the olefin. As a result, control of stereoselectivity in this process appears to be mediated by the existence or absence of forced Pt/Mn metal –metal proximity.

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# 1. Introduction

Cooperativity of transition metals in catalysis is one of the most intriguing and unsolved phenomena at the molecular level. Although many transition-metal-mediated processes utilize monometallic catalysts, many successful variants employ the use of two metals instead of one to exploit aspects of "metal-metal cooperativity", such as, for example, in the catalytic desulfurization of oil using Co/Mo [1,2] and Ni/Mo systems [3]. Unfortunately however, the origin of these cooperative effects is far from being understood, although there have been significant recent advances [4–13]. In our group, reactions involving heterocyclic ring-opening processes are of significant interest since they provide invaluable routes to many important organic compounds [14–17]. In particular, the cleavage of carbon-sulfur bonds in S-heterocycles attracts considerable attention in transition-metal catalysis [18], owing to the ubiquitous nature of this process in the study of materials and pharmacological products [19]. To this effect, molecular dinuclear complexes may offer a unique opportunity to model many of these C-S bond cleavage processes.

We previously reported the synthesis of a series of heterodinuclear organoplatinum-manganese complexes having both Pt-Mn and M-C bonds [(dppe)RPt-M(CO)<sub>5</sub>] (dppe = 1,2bis(diphenylphosphino)ethane, R = Me, Et; M = Mn, Re) by metathesis of [(dppe)PtRX] with Na[M(CO)<sub>5</sub>]. Upon reaction with cis- and trans-2,3-dimethylthiirane, these complexes cleanly promoted C-S bond cleavage with inversion of stereochemistry to give the corresponding (thiametallacycle)platinum complexes, which upon heating resulted in desulfurization to produce the respective trans- and cis-2-butenes (Scheme 1) [20]. During our continuous studies, we serendipitously discovered an unexpected structural feature when this system contains a neopentyl group  $(R = Np, -CH_2CMe_3)$  where an *acyl* moiety is formed and subsequently acts as a bridging ligand between the Pt–M linkage. In this communication, we wish to report the unique aspects of the new Pt-Mn heterodinuclear complex, where this ancillary bridging ligand forces complete retention of configuration in C-S bond cleavage of thiiranes caused by cooperativity of the Pt and Mn metals, while related dinuclear complexes without this bridging ligand show inversion of configuration in these reactions.

# 2. Results and discussion

Using methods and conditions similar to those used to generate the non-bridged methyl and ethyl complexes [20], the new acylbridged Pt/Mn complex  $[(dppe)Pt(\mu-C(O)Np-1\kappa C, 2\kappa O)-Mn(CO)_4]$ 



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Scheme 1. Reaction of Pt/Mn species with substituted thiirane to produce alkene with inversion of stereochemistry.

(2) was prepared in 82% yield from the mononuclear Pt species 1 (Scheme 2). The isolation of single crystals of 2 allowed us to deduce a *bridging* geometry as shown in Fig. 1. In the generation of 2 from 1, the neopentyl group is considered to migrate from platinum to the manganese atom upon generation of the Pt–Mn bond, most likely due to steric congestion at Pt caused between the proximal Ph groups of the dppe ligand and the bulky neopentyl group itself. Along with electronic factors associated with the neopentyl group being strongly electron-donating, facile CO insertion can generate a less bulky acyl group -C(O)Np, which can subsequently migrate back to Pt and coordinate to Mn *via* the carbonyl oxygen atom to occupy its vacant site, inherently locking it into close proximity. Such a unique and facile insertion process, including organic group transfer along Pt–M bonds, has been proposed by us previously [21].

The acyl group on platinum forms a bridge between the two metals, locking them into close proximity (Pt–Mn = 2.607(1) Å), especially when compared to non-bridged cases such as in [(dppe) MePt–Mn(CO)<sub>5</sub>] (2.795(2) Å) [20]. The oxygen atom from the acyl group is firmly bound to Mn, forming a planar four-membered metallacycle (Mn–O(1) = 2.070(6) Å), since the sum of the internal angles about Pt–C(36)–O(1)–C(1) is 360°. Spectroscopically, the resonance representing the phosphorus *trans* to the manganese atom exhibits much weaker coupling to <sup>195</sup>Pt ( $^{1}J_{P-Pt}$  = 2230 Hz) compared to the aforementioned methyl and ethyl systems ( $^{1}J_{P-Pt}$  = 3267 Hz) [20], which suggests that the *trans* influence of the manganese group is clearly weakened by this "locked" geometry.

As shown in Scheme 3, the bridged species **2** reacts with *trans*and *cis*-2,3-dimethylthiirane at 50 °C in a different way than the terminal methyl and ethyl variants, releasing *trans*- and *cis*-2butene in 90% and 89% yield, respectively. This *direct* desulfurization of thiiranes does not display any appreciable solvent effect, advancing at identical rates in both benzene and acetone. Furthermore, when desulfurization was attempted with a variety of other thiiranes, namely 2-methylthiirane, thiirane, 7-thiabicyclo [4.1.0]heptane, and 2,2-dimethylthiirane, the rate of conversion did not change significantly, even when much more bulky thiiranes were used (see Supplementary data). The resulting organometallic



Scheme 2. Synthesis of bridged species 2.

species was found to be the thiocarboxylato species **3**, as confirmed by X-ray structure analysis as shown in Fig. 2.

In this structure, the Pt and Mn atoms reside in extremely strained square planar and octahedral geometries, respectively, as



**Fig. 1.** Three-dimensional representation of bridged species  $[(dppe)Pt(\mu-C(0)Np-1\kappaC,2\kappaO)-Mn(CO)_4]$  (2) showing the numbering scheme. Thermal ellipsoids are shown at the 50% probability level, except for hydrogen atoms, which are placed at the calculated positions based on the riding model. Hydrogen atoms on the dppe and methyl groups are not shown. Only the ipso carbons of the dppe phenyl rings are shown. Relevant parameters (distances in Å and angles in deg.): Pt-Mn = 2.607(1), Pt-P(1) = 2.284(2), Pt-P(2) = 2.319(2), Pt-C(1) = 2.022(8), Mn-O(1) = 2.070(6), C(1)-O(1) = 1.261(9); P(1)-Pt-Mn = 169.97(5), P(2)-Pt-C(1) = 173.9(3), Pt-Mn-C(35) = 176.1(3), Mn-Pt-C(1)-O(1) = -0.3(5)



Scheme 3. Desulfurization of thiiranes using bridged (2) or non-bridged (4) species.



**Fig. 2.** Three-dimensional representation of thiocarboxylato-bridged platinum/manganese species [(dppe)Pt( $\mu$ -SC(O)Np)–Mn(CO)<sub>4</sub>] (**3**) showing the numbering scheme. Thermal ellipsoids are as described as in Fig. 1. Hydrogen atoms on methyl groups are not shown. Only the ipso carbons of the dppe phenyl rings are shown. Relevant parameters (distances in Å and angles in deg.): Pt–Mn = 2.6511(4), Pt–P(1) = 2.2819(7), Pt–P(2) = 2.2353(6), Pt–S = 2.3179(6), Mn–S = 2.2908(7), Mn–C(33) = 1.850(3), Mn–C(34) = 1.805(3), Mn–C(35) = 1.799(3), Mn–C(36) = 1.838(4); P(1)–Pt–Mn = 163.89(2), P(2)–Pt–S = 159.87(3), Pt–Mn–C(34) = 156.50(9), S–Mn–C(35) = 158.7(1), C(33)–Mn–C(36) = 171.6(1).

indicated by the particularly bent angles at Pt (P(1)–Pt– Mn = 163.89(2)°, P(2)–Pt–S = 159.87(3)°) and Mn (Pt–Mn– C(34) = 156.50(9)°, S–Mn–C(35) = 158.7(1)°). This kind of strain is similar to that in other octahedral thiocarboxylato-bridged complexes [22]. Although the Pt and Mn atoms are further separated compared to **2**, the distance is still suggestive of a Pt–Mn single bond.

The progress of this reaction was monitored at 30 °C in a large excess of *trans*-2,3-dimethylthiirane, providing first order kinetics. A linear dependence of the first order rate constant  $k_{obs}$  vs. thiirane concentration as well as the negligible solvent effect highly suggest a bimolecular concerted pathway (Scheme 4).

In order to test our hypothesis that this retention behavior is most likely due to the unique bridging structure of 2, we investigated strategies to transform 2 into an analogous non-bridged species, which would facilitate the desulfurization with *inversion* of stereochemistry. Thus, the introduction of CO gas in a benzene solution of 2 smoothly replaced the coordinated acyl oxygen on Mn by CO, generating an opened acyl product [(dppe)(NpC(O))Pt-Mn(CO)<sub>5</sub>] (**4**), analogous to the non-bridged methyl and ethyl species noted previously. However, unless the solution of **4** is kept under CO atmosphere, it begins to convert back to **2** in less than 1 h. This reversibility indicates that these two species are in equilibrium in the presence of  $CO_{(g)}$ .

With this new acyl non-bridged species in hand, we tested whether complex **4** would also facilitate the desulfurization of thiiranes with inversion of stereochemistry, despite the electronic differences imparted by the acyl group compared to non-bridged methyl and ethyl variants. As expected, on treatment with cisand trans-2,3-dimethylthiirane at room temperature, complex 4 produces the anti- and syn-thiamanganacyclic complexes 5, respectively, analogous to the methyl and ethyl systems [20] (Scheme 3). This in turn helps support our hypothesis of the bridged vs. non-bridged dichotomy dictating stereochemistry of the released olefin. Furthermore, although reaction of the bridged species 2 with thiiranes did exhibit signs of an appreciable solvent effect, the rate of the reaction of **4** is clearly accelerated by polar solvents, which is consistent with an S<sub>N</sub>2 process for this initial C-S bond cleavage event of desulfurization by non-bridged dinuclear Pt/Mn complexes. This process most likely proceeds via a cationic intermediate after dissociation of the  $Mn(CO)_{5}^{-}$  moiety, followed by coordination of thiirane to Pt as previously noted. An X-ray diffraction study of 5<sub>anti</sub> unequivocally confirms our structural hypothesis (Fig. 3).

Heating of these *syn*- and *anti*-thiamanganacyclic species at 75 °C results in the liberation of *cis*- and *trans*-2-butene, respectively, in quantitative yields. Interestingly, the fate of the organometallic complex is identical to that from the bridged species **2** (Scheme 3), as made evident by identical spectral parameters. However, **2** obviously transforms into **3** *via* a very different mechanism (*vide infra*). Although transformation of **4** to **5** proceeded with inversion, this second step appears to continue with complete retention of stereochemistry and indicates no solvent effect. Furthermore, analysis of the headspace at the conclusion of this reaction confirmed the stoichiometric release of  $CO_{(g)}$ , as detected by GC.

With the data represented in this report, we can conclude that this new "bridged" neopentyl analog **2** undergoes a different process for desulfurization of thiiranes owing to the fact that an acyl bridge is present to force metal—metal proximity. The consequences of this effect appear to be twofold: 1) the manganese carbonyl moiety is unable to easily dissociate to allow thiirane coordination to platinum, and facilitate subsequent  $S_N2$  attack by Mn in the S-heterocyclic backbone, and 2) it allows for a "forced" model of metal—metal cooperativity with the metals chained together by an acyl group, effecting a different concerted



Scheme 4. Proposed concerted pathway for desulfurization of thiiranes using bridged species 2.



**Fig. 3.** Three-dimensional representation of *anti*-thiamanganacyclic platinum species [(dppe)(NpC(O))Pt(*trans*-SCH(Me)CH(Me)CO)Mn(CO)<sub>4</sub>] (**5**<sub>*anti*</sub>) showing the numbering scheme. Thermal ellipsoids are as described in Fig. 1, except for hydrogen atoms, which are placed at the calculated positions based on the riding model. Hydrogen atoms on methyl groups are not shown. Only the ipso carbons of the dppe phenyl rings are shown. Relevant parameters (distances in Å and angles in deg.): Pt–S = 2.372(2), Pt–P(1) = 2.573(2), Pt–P(2) = 2.343(2), Pt–C(1) = 2.057(8), Mn–S = 2.375(2), C(1)–O(1) = 1.21(1); P(1)–Pt–S = 172.72(7), P(2)–Pt–C(1) = 174.4(3), S–Mn–C(41) = 168.6(4), C(37)–Mn–C(38) = 178.7(4), C(39)–Mn–C(40) = 168.0(4).

desulfurization process, which is likely similar to the desulfurization mechanism postulated by Bergman, et al. in heterodinuclear Ir/Zr systems [23]. Owing to our isolation of the final organometallic species in this process, the bridging thiocarboxylato structure **3**, we propose our own variant to this mechanism. In this process, the bridged species 2 undergoes a concerted bond-breaking-andmaking step to yield the olefin with retention of stereochemistry. The resulting µ-sulfido, µ-acyl complex could then undergo reductive elimination to form a new sulfur linkage to the acyl moiety, while producing two mononuclear components. From here, oxidative addition of the Mn-S bond to the Pt center could generate a new  $\mu$ - $\kappa^2$ S,O-thiocarboxylato ligand, which can rearrange to form the thiocarboxylato species 3. In strong support of this hypothesis, similar rates for the reaction of 2 with a variety of different thiiranes suggests that the difference in steric bulk has little-to-no steric effect, which is made evident by the distance of the substituents from the active site in our mechanism. An analogous mechanism may be in effect during the transformation of **5** into **3** following the concerted liberation of olefin, presumably through the same proposed (µ-sulfido)(acyl)platinum intermediate.

## 3. Conclusions

The forced-proximity in a heterodinuclear Pt/Mn complex inhibits dissociation of the Mn moiety, preventing  $S_N2$  reactivity with thiiranes, and proceeds to undergo C–S bond cleave *via* retention of stereochemistry. Kinetic analyses support a concerted, bimolecular pathway. The acyl bridge can be released by coordination of another CO ligand to Mn, which results in a terminal acyl species with an unsupported metal–metal bond. This species exhibits similar reactivity to the previously-reported methyl and ethyl cases, facilitating desulfurization of thiiranes with inversion of stereochemistry. Further studies, involving detailed kinetics to clarify the mechanism of this direct desulfurization process, as well as investigations to potentially make these systems catalytic are in progress.

#### 4. Experimental

## 4.1. General comments

All manipulations were carried out under a dry nitrogen or argon atmosphere using standard Schlenk techniques. All solvents were dried over and distilled from appropriate drying agents under N<sub>2</sub>. The NMR spectra were recorded on a JEOL ECX400P (399.8 MHz for <sup>1</sup>H, 161.8 MHz for <sup>31</sup>P). The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} chemical shifts are referenced to TMS and external 85% H<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O, respectively. The IR spectra were recorded on a JASCO FT/IR-4100 spectrometer using KBr disks. Elemental analyses were carried out using a Perkin–Elmer 2400 series II CHN analyzer. Both *cis*- and *trans*-2,3-dimethylthiirane were prepared by literature procedures [24]. The species [(dppe) PtNpCl] (**1**) [25], tetramethylthiirane [26], and Na[Mn(CO)<sub>5</sub>] [27,28] were prepared as reported previously. All other chemicals were obtained from commercial sources and used directly without further purification. Details of time-course experiments and X-ray analyses are described in the Supplementary data.

#### 4.1.1. $[(dppe)Pt(\mu-C(O)Np-1\kappa C, 2\kappa O)-Mn(CO)_4]$ (2)

A 30 mL portion of THF was added to a flask containing 1 (0.607 g, 0.867 mmol) and AgNO<sub>3</sub> (0.182 g, 1.069 mmol). The resulting solution was stirred in the dark overnight, resulting in a pink-colored slurry. The yellow solution was separated from the pink precipitate by filtered cannula, and added to a second flask containing a stirring 10 mL green THF solution of Na[Mn(CO)<sub>5</sub>] (0.275 g, 1.260 mmol) at  $-30 \,^{\circ}\text{C}$ , turning the resulting solution orange in color. The solution was further stirred at -30 °C for 4 h and the solvent was removed in vacuo. The red oily solid was dried, then redissolved in 10 mL of benzene. The insoluble impurities were separated by filtered cannula and the solvent was removed in vacuo. The red solid was redissolved in 4 mL of THF and recrystallized by slow diffusion of 10 mL of layered hexane at -30 °C. The resulting crystals were washed with  $3 \times 5$  mL portions of benzene, redissolved in 7 mL of benzene, and passed through a small Soxhlet filter. Solvent was removed in vacuo and the solid recrystallized from THF and hexane, washed with hexane, and dried in vacuo, giving bright orange crystals (0.554 g, 74%). <sup>1</sup>H NMR (399.78 MHz, benzene-d<sub>6</sub>, 18.0 °C), δ 7.73 (m, 4H), 7.51 (m, 4H), 7.15 (m, 10H), 7.01 (m, 2H, dppe<sub>Ph</sub>); 2.32 (m, 2H, Np<sub>CH<sub>2</sub></sub>); 1.91 (m, 2H), 1.72 (m, 2H, dppe<sub>CH<sub>2</sub>CH<sub>2</sub>); 0.72 (s, 9H, Np<sub>Me</sub>).  ${}^{31}P{}^{1}H$  NMR (161.83 MHz, ben-</sub> zene- $d_6$ , 18.0 °C),  $\delta$  53.4 (d, 1P,  ${}^2J_{P-P} = 16$  Hz,  ${}^1J_{P-Pt} = 2117$  Hz, P–Pt– Mn); 49.2 (d, 1P,  ${}^{2}J_{P-P} = 16$  Hz,  ${}^{1}J_{P-Pt} = 1943$  Hz, P–Pt–C(O)Np). IR (KBr, cm<sup>-1</sup>): 2046, 2002, 1907, 1869. Anal. Calcd for C<sub>36</sub>H<sub>35</sub>MnO<sub>5</sub>P<sub>2</sub>Pt: C, 49.62; H, 3.88. Found: C, 50.30; H, 4.10.

# 4.1.2. $[(dppe)Pt(\mu-SC(O)Np)-Mn(CO)_4]$ (3)

Route 1: A 4 mL portion of benzene was added to a flask containing 2 (0.165 g, 0.191 mmol). The resulting solution was stirred for 10 min at room temperature, followed by rapid injection of trans- (or cis-)2,3-dimethylthiirane (20 µL, 0.22 mmol). The solution was heated to 50 °C and stirred for 2 h, wherein it changed from bright to dark orange. The solution was filtered via cannula into 5 mL of hexane. The heterogeneous mixture was filtered again via cannula, and the black precipitate discarded. Solvent was removed in vacuo and the sample redissolved in 1 mL of THF, and recrystallized by layering 10 mL of hexane and storing at -30 °C overnight, giving a dark orange powder. The sample was washed with  $5 \times 5$  mL portions of hexane before drying *in vacuo*, giving a dark orange crystalline material (0.145 g, 85%). Route 2. A 4 mL portion of benzene was added to a flask containing 5<sub>syn</sub> (or 5<sub>anti</sub>) (0.115 g, 0.130 mmol). The resulting solution was heated to 50 °C and stirred for 2 h, wherein it changed from dark yellow to dark orange. The solution was filtered via cannula into 5 mL of hexane. Solvent was removed *in vacuo* and purified as in Route 1, giving a dark orange crystalline material (0.145 g, 89%). <sup>1</sup>H NMR (399.78 MHz, C<sub>6</sub>D<sub>6</sub>, 18.6 °C):  $\delta$  7.67 (br m, 6H), 7.08 (m, 14H, dppe<sub>Ph</sub>); 2.01–1.73 (m, 4H, dppe<sub>CH2CH2</sub>); 1.55 (s, 2H, Np<sub>CH2</sub>); 0.87 (s, 9H, Np<sub>Me</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161.83 MHz, C<sub>6</sub>D<sub>6</sub>, 19.0 °C),  $\delta$  60.7 (s, 1P, <sup>1</sup>J<sub>P-Pt</sub> = 4053 Hz, P–Pt–S); 59.7 (s, 1P, <sup>1</sup>J<sub>P-Pt</sub> = 2871 Hz, P–Pt–Mn).

#### 4.1.3. [(dppe)(NpC(O))Pt-Mn(CO)<sub>5</sub>] (4)

A 5 mL portion of benzene was added to a flask containing 2 (0.506 g, 0.589 mmol). The resulting solution was cooled to -196 °C, and the headspace removed in vacuo. The solution was allowed to warm to room temperature, at which point the headspace was filled with an atmosphere of CO<sub>(g)</sub>. The solution was stirred overnight, wherein it changed from dark red to a bright vellow color. The solvent was removed and the crude product dried under vacuum, giving a vellow powder. The crude sample was redissolved in 5 mL of THF, and recrystallized by layering 20 mL of hexane and storing at -30 °C overnight, giving a bright yellow powder. The sample was washed with  $5 \times 5$  mL portions of hexane before drying in vacuo, giving a bright yellow crystalline material (0.510 g, 98%). <sup>1</sup>H NMR (399.78 MHz, C<sub>6</sub>D<sub>6</sub>, 21.9 °C): δ 8.07 (br m, 4H), 7.73 (m, 4H), 7.62 (br m, 4H), 7.00 (br m, 8H, dppe<sub>Ph</sub>); 2.10 (m, 2H), 1.77 (m, dppe<sub>CH2CH2</sub>); 1.54 (s, 2H, Np<sub>CH2</sub>); 0.89 (s, 9H, Np<sub>Me</sub>). <sup>31</sup>P {<sup>1</sup>H} NMR (161.83 MHz, C<sub>6</sub>D<sub>6</sub>, 21.9 °C),  $\delta$  39.3 (s, 1P, <sup>1</sup>J<sub>P-Pt</sub> = 3568 Hz, P-Pt-Mn); 36.1 (s, 1P,  ${}^{2}J_{P-Pt} = 16$  Hz,  ${}^{1}J_{P-Pt} = 1338$  Hz, P-Pt-C(O) Np). IR (KBr, cm<sup>-1</sup>): 1619 (s, C=O).

# 4.1.4. [(dppe)(NpC(O))Pt(cis-SCH(Me)CH(Me)CO)Mn(CO)<sub>4</sub>] (5<sub>syn</sub>)

A 5 mL portion of benzene was added to a flask containing 4 (0.100 g, 0.113 mmol). The resulting solution was stirred for 10 min at room temperature, followed by rapid injection of trans-2,3dimethylthiirane (15 µL, 0.17 mmol). The solution was stirred overnight, wherein it changed from bright to dark yellow. The solvent was removed and the crude product washed with 5  $\times$  5 mL portions of hexane before being dried under vacuum, giving a dark vellow powder. The crude sample was redissolved in 2 mL of benzene, and recrystallized by layering 10 mL of diethyl ether and 10 mL of hexane and storing at -30 °C overnight, giving a dark yellow powder. The sample was washed with 5  $\times$  5 mL portions of hexane before drying in vacuo, giving a dark yellow crystalline material (0.086 g, 78%). <sup>1</sup>H NMR (399.78 MHz, acetone-*d*<sub>6</sub>, 22.1 °C):  $\delta$  8.21 (br m, 4H), 7.70 (m, 4H), 7.49 (br m, 4H), 7.43 (br m, 8H, dppe<sub>Ph</sub>); 3.09 (br, 1H, CH); 2.55–2.67 (m, 4H, dppe<sub>CH2CH2</sub>); 1.44 (br, 1H, CH); 1.43 (s, 2H, Np<sub>CH<sub>2</sub></sub>); 1.12 (d, 3H,  ${}^{3}J_{H-H} = 6.7$  Hz, Me); 0.81 (s, 9H, Np<sub>Me</sub>); 0.76 (d, 3H,  ${}^{3}J_{H-H} = 6.5$  Hz, Me).  ${}^{31}P{}^{1}H$  NMR (161.83 MHz, acetone- $d_6$ , 22.5 °C),  $\delta$  34.3 (s, 1P,  ${}^1J_{P-Pt}$  = 3575 Hz, P– Pt–S); 32.9 (s, 1P,  ${}^{1}J_{P-Pt} = 1320$  Hz, P–Pt–C(O)Np).

# 4.1.5. [(dppe)(NpC(O))Pt(trans-SCH(Me)CH(Me)CO)Mn(CO)<sub>4</sub>] (5<sub>anti</sub>)

The desired product was prepared and purified as described for **5**<sub>*syn*</sub> using **4** (0.101 g, 0.114 mmol) and *cis*-dimethylthiirane (15 µL, 0.165 mmol). The sample was washed with  $5 \times 5$  mL portions of hexane before drying *in vacuo*, giving a dark yellow crystalline material (0.081 g, 73%). <sup>1</sup>H NMR (399.78 MHz, acetone-*d*<sub>6</sub>, 22.1 °C):  $\delta$  8.26 (br m, 4H), 7.63 (m, 4H), 7.53 (br m, 4H), 7.47 (br m, 8H, dppe<sub>Ph</sub>); 2.48–2.84 (m, 4H, dppe<sub>CH<sub>2</sub>CH<sub>2</sub>); 2.23 (dq, 1H, <sup>3</sup>*J*<sub>H</sub>–H = 12.1 Hz, <sup>3</sup>*J*<sub>H</sub>–H = 6.4 Hz), 1.91 (dq, 1H, <sup>3</sup>*J*<sub>H</sub>–H = 12.1 Hz, <sup>3</sup>*J*<sub>H</sub>–H = 6.4 Hz, CH); 1.54 (s, 2H, Np<sub>CH<sub>2</sub></sub>); 1.54 (d, 3H, <sup>3</sup>*J*<sub>H</sub>–H = 6.4 Hz, Me); 0.67 (s, 9H, Np<sub>Me</sub>). <sup>31</sup>P[<sup>1</sup>H} NMR (161.83 MHz, acetone-*d*<sub>6</sub>, 22.3 °C),  $\delta$  34.3 (s, 1P, <sup>1</sup>*J*<sub>P</sub>–Pt = 3545 Hz, P–Pt–S); 31.5 (s, 1P, <sup>1</sup>*J*<sub>P</sub>–Pt = 1329 Hz, P–Pt–C(O)Np).</sub>

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#### Appendix A. Supplementary material

CCDC Nos. 922487 (for **2**), 922489 (for **3**), and 922488 (for **5**<sub>*anti*</sub>), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam. ac.uk/data\_request/cif.

#### Appendix B. Supplementary data

Figures depicting the solvent dependence of the rate in the reaction of **2** and **4** with *trans*-2,3-dimethylthiirane, sample pseudo first order plots of the reaction of the bridged species with various amounts of *trans*-2,3-dimethylthiirane; as well as tables of crystallographic experimental details for 2, 3, and 5<sub>anti</sub>. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.04.003.

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