

# “ $\beta$ -*cis*-SAr effect” on decarbonylation from $\alpha,\beta$ -unsaturated acyl and aroyl complexes†

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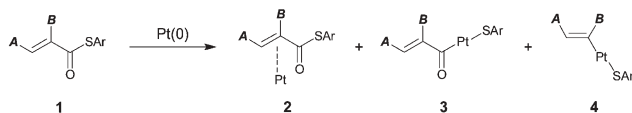
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Lone pair of heteroatom located at the  $\beta$ -*cis* position in  $\alpha,\beta$ -unsaturated acyl and aroyl group 10 metal complexes dramatically facilitated the stoichiometric and catalytic decarbonylation reactions.

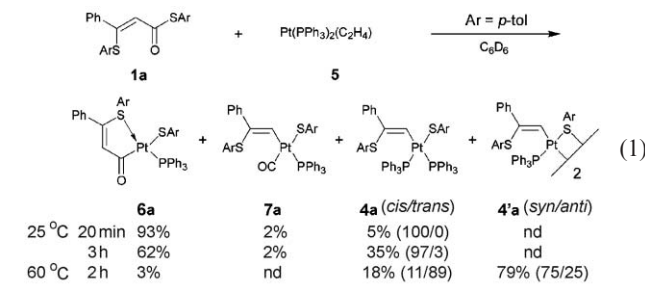
Revealing how to activate organic compounds in collaboration with metal complexes is one of the most fascinating topics in current chemistry.<sup>1</sup> Now it is well-acknowledged that the coordination of a lone pair of heteroatoms to metals can direct and facilitate various types of reactions represented by the oxidative addition of inert bonds to low-valent transition-metal complexes.<sup>2</sup> Herein we wish to report on a novel type of activation utilizing the coordination of a lone pair on sulfur to metals: the decarbonylation from  $\alpha,\beta$ -unsaturated acyl and aroyl complexes.

Recently, we have disclosed that substituent effects on the reactions of  $\alpha,\beta$ -unsaturated carbonyl compounds with low-valent metals were clearly elicited by exploiting fine-tunable reactivity of the C–S bond of thioester **1** having substituents at *A* and *B* toward platinum(0)-complex to give  $\pi$ -complex **2** and acyl complex **3**, which can potentially lead to the formation of vinyl complex **4** (Scheme 1).<sup>3</sup>



Scheme 1

During the course of further endeavors to understand the substituent effects, the reaction of (*Z*)-(Ph)(*p*-tolS)C=CHC(O)-(Stol-*p*) (**1a**) (0.022 mmol) with Pt(PPh<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>) (**5**) (0.020 mmol) was examined in C<sub>6</sub>D<sub>6</sub> (0.5 mL) at 25 °C using S=P(C<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>3</sub> as an internal standard (eqn (1)).



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The <sup>1</sup>H NMR spectrum taken after 20 min indicated the formation of a platinum complex **6a** by a couple of Me singlets at  $\delta$  1.72 and  $\delta$  2.18 as well as a vinyl singlet at  $\delta$  6.35 with  $J_{\text{Pt-H}} = 28.8$  Hz in 93% yield and its <sup>31</sup>P NMR spectrum showed the formation of 2% of suspected CO-coordinated vinylplatinum complex **7a** (*vide infra*) and 5% of *cis*-Pt[(*Z*)-CH=C(Stol-*p*)-(Ph)](Stol-*p*)(PPh<sub>3</sub>)<sub>2</sub> (*cis*-**4a**).<sup>4</sup> It must be noted that the signals of **2a**, **3a** and even **6a** and free PPh<sub>3</sub> were not detected by <sup>31</sup>P NMR under the present conditions. The yield of **4a** increased to 35% yield after 3 h and additional heating at 60 °C for 2 h resulted in the formation of **4a** and **4'a** (dimeric form of **4a**) in good combined yields (97%).<sup>5</sup> In stark contrast, the reaction of (*E*)-PhC(H)=CHC(O)(Stol-*p*) (**1b**) with **5** generated **2b** and **3b** as major products<sup>3</sup> and only a trace amount of the corresponding vinylplatinum complex *trans*-Pt[(*E*)-C(H)=CH(Ph)](Stol-*p*)(PPh<sub>3</sub>)<sub>2</sub> (*trans*-**4b**) (0.5%) was furnished after 3 h at 25 °C and heating the solution at 60 °C for 5 h resulted in the formation of a complicated mixture, which included 13% of *trans*-**4b**.<sup>6</sup>

With respect to **6a**, a good crystal suitable for X-ray crystallographic analysis was gratifyingly obtained from chlorobenzene/pentane solution, and its ORTEP diagram is shown in Fig. 1, demonstrating that **6a** was the acyl complex with  $\beta$ -*cis*-SAr coordination to Pt. The S–Pt distance was 2.32 Å, much shorter than the sum of van der Waals radii (3.55 Å)<sup>7</sup> and the five-membered ring lay almost coplanar with the Pt(II) square plane.<sup>8</sup>

The <sup>31</sup>P NMR spectra of the crystal of **6a** dissolved in C<sub>6</sub>D<sub>6</sub> showed two singlets at  $\delta$  30.0 ( $J_{\text{Pt-P}} = 4571$  Hz) and  $\delta$  17.5 ( $J_{\text{Pt-P}} = 1737$  Hz) in a ratio of 92 : 8. The former was ascribed to **6a**, in

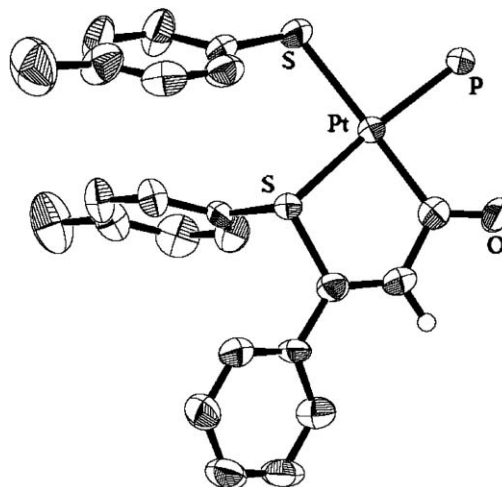
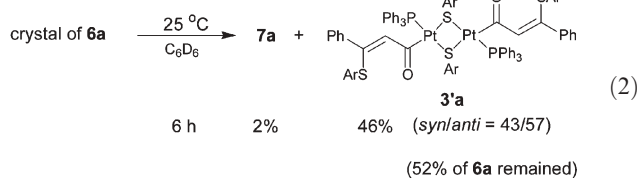
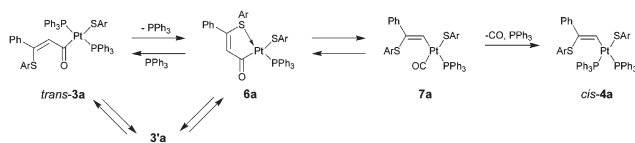


Fig. 1 ORTEP diagram of **6a** (Ph on PPh<sub>3</sub> omitted).

which weak intramolecular  $\beta$ -*cis*-SAr coordination induced a significantly large  $J_{\text{Pt-P}}$  value. The latter signal can be tentatively assigned to  $\text{Pt}[(Z)\text{-C}(\text{H})=\text{C}(\text{Stol-}p)(\text{Ph})](\text{Stol-}p)(\text{PPh}_3)(\text{CO})$  (**7a**) judging from the  $J_{\text{Pt-P}}$  value<sup>9</sup> and CO stretching ( $2065\text{ cm}^{-1}$ ) of IR spectrum in solution.<sup>10</sup> Leaving the sample at  $25\text{ }^\circ\text{C}$  gradually produced dimeric acyl platinum **3'a**<sup>3</sup> in 46% after 6 h (eqn. (2)).



On the other hand, when a catalytic amount of  $\text{PPh}_3$  (0.26 equiv.) was added into the solution of the crystal of **6a**, only the signals of **7a** (4%) and *cis*-**4a** (5%) were detected at  $25\text{ }^\circ\text{C}$ , while the signal of **6a** (82%) was clearly detected by the  $^1\text{H}$  NMR spectrum.



Scheme 2

Taking the foregoing facts into account, after the formation of *trans*-**3a**,  $\beta$ -*cis*-SAr would promptly coordinate to Pt to generate **6a** overwhelmingly (Scheme 2). In the presence of free  $\text{PPh}_3$ , there would be fast interconversion between *trans*-**3a** and **6a**, although, probably due to the entropic factor, the equilibrium between *trans*-**3a** and **6a** strongly leaned to the side of **6a** at  $25\text{ }^\circ\text{C}$ .<sup>11</sup> This is why the signals of **6a**, free  $\text{PPh}_3$  and a trace amount of *trans*-**3a** were submerged into the baseline of the  $^{31}\text{P}$  NMR chart, although the  $^1\text{H}$  NMR signals of Me and vinyl of **6a** were hardly affected by this exchange. The vinyl moiety of **6a** would migrate onto Pt with the assistance of  $\beta$ -*cis*-SAr coordination to generate **7a**, which was gradually trapped by  $\text{PPh}_3$  to afford vinylplatinum *cis*-**4a** as a kinetic product.<sup>12,13,4</sup> In the absence of free  $\text{PPh}_3$ , **6a** (or *via* trace amount of **3a**) would slowly produce dimeric **3'a**.

Furthermore, the utility of the present " $\beta$ -*cis*-SAr effect" was attested by catalytic decarbonylation of **1** (Table 1).<sup>14,15</sup>

In contrast to the fact that no decarbonylation of **1b** ( $A = \text{Ph}$ ,  $C = \text{H}$ ) took place in the presence of 5 mol% of  $\text{Pd}(\text{PPh}_3)_4$  under benzene reflux for 5 h (Entry 1), **1a** successfully underwent

Table 1 The Pd-catalyzed decarbonylation of **1**<sup>a</sup>

		$\text{Ar-C}(\text{O})\text{Stol-}p$		$\text{Ar-C}(\text{O})\text{Stol-}p$		
		<b>1</b>		<b>8</b>		
Entry	<b>1</b>	<i>A</i>	<i>C</i>	Time/h	<b>8</b>	Yield (%) <sup>b</sup>
1	<b>1b</b>	Ph	H	5	<b>8b</b>	0
2	<b>1a</b>	Ph	<i>p</i> -tolS	1	<b>8a</b>	98
3	<b>1c</b>	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	<i>p</i> -tolS	3	<b>8c</b>	95
4	<b>1d</b>	<i>p</i> -tolS	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	3	<b>8d</b>	6

<sup>a</sup> **1** (0.5 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (5 mol%) under  $\text{C}_6\text{H}_6$  (0.5 mL) reflux.  
<sup>b</sup> Isolated yield.

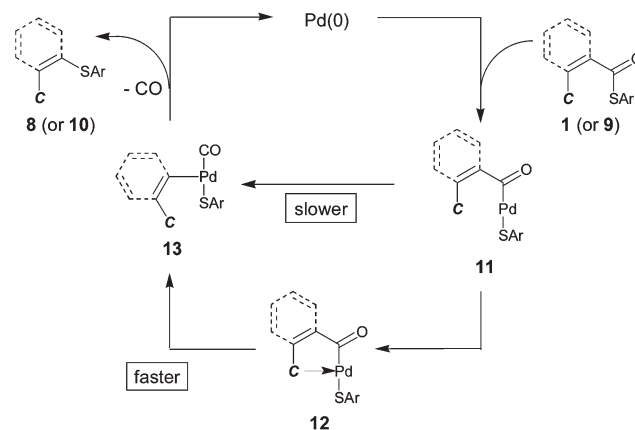
Table 2 The Pd-catalyzed decarbonylation of **9**<sup>a</sup>

		$\text{Ar-C}(\text{O})\text{Stol-}p$		$\text{ArStol-}p$	
		<b>9</b>		<b>10</b>	
Entry	<b>9</b>	<i>Ar</i>	<b>10</b>	Yield (%) <sup>b</sup>	
1	<b>9a</b>	Ph	<b>10a</b>	10	
2	<b>9b</b>	<i>o</i> -PhSC <sub>6</sub> H <sub>4</sub>	<b>10b</b>	97	
3	<b>9c</b>	<i>p</i> -PhSC <sub>6</sub> H <sub>4</sub>	<b>10c</b>	10	
4	<b>9d</b>	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>10d</b>	71	
5	<b>9e</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>10e</b>	13	
6	<b>9f</b>	<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub>	<b>10f</b>	92	
7	<b>9g</b>	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	<b>10g</b>	3	

<sup>a</sup> **9** (0.5 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (5 mol%) under toluene (0.5 mL) reflux for 1 h. <sup>b</sup> Isolated yield.

decarbonylation to produce the corresponding vinylsulfide **8a** in 98% yield after 1 h (Entry 2). Similar results were also obtained when *n*-C<sub>6</sub>H<sub>13</sub> and SAr were introduced at *A* and *C* to form the corresponding vinylsulfide **8c** in 95% yield after 3 h (Entry 3), while the decarbonylation hardly proceeded when **1d** ( $A = \text{Stol-}p$ ,  $C = n\text{-C}_6\text{H}_{13}$ ), the stereoisomer of **1c**, was employed as a substrate (6% of **8d**) (Entry 4). Moreover, the generality of the present principle was validated using decarbonylation of arylthioester  $\text{ArC}(\text{O})\text{Stol-}p$  (**9**) (Table 2).

As expected, the dramatic facilitation of decarbonylation was observed by introducing *o*-SPh (**9b**) to produce **10b** in 97% yield, although **9a** ( $\text{Ar} = \text{Ph}$ ) and **9c** ( $\text{Ar} = p\text{-SPh}$ ) underwent decarbonylation only in 10% in both cases (90% of **9a** and **9c** both recovered) (Entries 1–3). Intriguingly, the present prototype was not confined to the  $\beta$ -*cis*-SAr group. Significant (Entry 4 *vs.* Entry 5) and quite remarkable (Entry 6 *vs.* Entry 7) facilitation was also shown by *o*-Cl and *o*-MeO groups. A possible reaction route of the present palladium-catalyzed decarbonylation is shown in Scheme 3. After the oxidative addition of **1** (or **9**) to the  $\text{Pd}(0)$ -complex took place to form **11**, the lone pair in *C* ( $C = \text{SAr}$ , Cl, OMe) would spontaneously coordinate to the Pd-center to form **12**. The decarbonylation, the rate-determining step of the whole Pd-catalyzed decarbonylation, would be much faster from **12** than that from **11** to afford vinyl or aryl palladium **13**, from which



Scheme 3 Proposed mechanism of the Pd-catalyzed decarbonylation of thioester.

**8** (or **10**) was reductively eliminated with the regeneration of the Pd(0)-complex.

In conclusion, this paper revealed that the lone pair of the heteroatom located at the  $\beta$ -*cis* position in  $\alpha,\beta$ -unsaturated acyl and aroyl group 10 metal complexes can significantly promote the decarbonylation process. Although the coordination of sulfur to metal has often been considered to suppress catalytic reactions,<sup>16</sup> the results described herein clearly substantiate that the sulfur functionality present at pertinent positions can rather effectively function as a powerful promoter.

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- It has been reported that stable metalacycles with similar fragments such as CpM[(Z)-C(O)C(E)=C(E)(SR)](CO)<sub>n</sub> (M = Fe, Mo, W; E = CF<sub>3</sub>, C(O)OMe) have been formed by cycloaddition reactions, see: (a) M. M. Kubicki, R. Kergoat, H. Scordia, L. C. Gomes de Lima, J. E. Guerchais and P. L'Haridon, *J. Organomet. Chem.*, 1988, **340**, 41; (b) M. M. Kubicki, L. C. Gomes de Lima, H. Scordia, J. E. Guerchais and P. L'Haridon, *J. Organomet. Chem.*, 1989, **367**, 143; (c) L. Carlton, J. L. Davidson and M. Shiralian, *J. Chem. Soc., Dalton Trans.*, 1986, 1577; (d) P. Veya, C. Floriani, A. Chiesi-Villa and C. Rizolli, *Organometallics*, 1993, **12**, 4646; (e) S. Lee, K. Cheung and W. Wong, *J. Organomet. Chem.*, 1995, **494**, 273 and references therein.
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- There can be two possible mechanisms. One is the migration of the vinyl moiety to a vacant coordination site of Pt(II)-complex **6a** and the other is a coplanar slippage of vinyl carbon to the  $\beta$ -*cis*-SAr coordination site with the C–S bond gradually cleaved.
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