" β -cis-SAr effect" on decarbonylation from α , β -unsaturated acyl and aroyl complexes[†]

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Lone pair of heteroatom located at the β -*cis* position in α , β -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.¹ 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.² 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 α,β -unsaturated acyl and aroyl complexes.

Recently, we have disclosed that substituent effects on the reactions of α , β -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 π -complex **2** and acyl complex **3**, which can potentially lead to the formation of vinyl complex **4** (Scheme 1).³



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(PPh₃)₂(C₂H₄) (5) (0.020 mmol) was examined in C₆D₆ (0.5 mL) at 25 °C using S=P(C₆H₄OMe-p)₃ as an internal standard (eqn (1)).



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The ¹H NMR spectrum taken after 20 min indicated the formation of a platinum complex 6a by a couple of Me singlets at δ 1.72 and δ 2.18 as well as a vinyl singlet at δ 6.35 with $J_{\text{Pt-H}}$ = 28.8 Hz in 93% yield and its ³¹P 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)- $(Ph)](Stol-p)(PPh_3)_2$ (*cis*-4a).⁴ It must be noted that the signals of **2a**, **3a** and even **6a** and free PPh₃ were not detected by 31 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%).⁵ In stark contrast, the reaction of (E)-PhC(H)=CHC(O)(Stol-p) (1b) with 5 generated 2b and 3b as major products³ and only a trace amount of the corresponding vinylplatinum complex trans-Pt[(E)-C(H)=CH(Ph)](Stol-p)(PPh₃)₂ (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.⁶

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 β -*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)⁷ and the fivemembered ring lay almost coplanar with the Pt(II) square plane.⁸

The ³¹P NMR spectra of the crystal of **6a** dissolved in C₆D₆ showed two singlets at δ 30.0 (J_{PLP} = 4571 Hz) and δ 17.5 (J_{PLP} = 1737 Hz) in a ratio of 92 : 8. The former was ascribed to **6a**, in



Fig. 1 ORTEP diagram of 6a (Ph on PPh₃ omitted).

which weak intramolecular β -cis-SAr coordination induced a significantly large J_{Pt-P} value. The latter signal can be tentatively assigned to $Pt[(Z)-C(H)=C(Stol-p)(Ph)](Stol-p)(PPh_3)(CO)$ (7a) judging from the J_{Pt-P} value⁹ and CO stretching (2065 cm⁻¹) of IR spectrum in solution.¹⁰ Leaving the sample at 25 °C gradually produced dimeric acyl platinum $3'a^3$ in 46% after 6 h (eqn. (2)).

crystal of **6a**
$$25 \, {}^{\circ}C$$
 $C_{6}D_{6}$ **7a** + Ph $\stackrel{Ph_{3}P}{\longrightarrow} Pi \stackrel{Ar}{\longrightarrow} Pi \stackrel{O}{\longrightarrow} Ph_{PPh_{3}}$ Ph
 $Ars O Ar$ (2)
6 h 2% 46% (*synlanti* = 43/57)
(52% of **6a** remained)

On the other hand, when a catalytic amount of PPh₃ (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 °C, while the signal of **6a** (82%) was clearly detected by the ${}^{1}H$ NMR spectrum.



Scheme 2	2
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Taking the foregoing facts into account, after the formation of trans-3a, β-cis-SAr would promptly coordinate to Pt to generate 6a overwhelmingly (Scheme 2). In the presence of free PPh₃, 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 $^{\circ}$ C.¹¹ This is why the signals of 6a, free PPh₃ and a trace amount of trans-3a were submerged into the baseline of the ³¹P NMR chart, although the ¹H 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 β -cis-SAr coordination to generate 7a, which was gradually trapped by PPh_3 to afford vinylplatinum *cis*-4a as a kinetic product.^{12,13,4} In the absence of free 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).^{14,15}

In contrast to the fact that no decarbonylation of 1b (A = Ph, C = H) took place in the presence of 5 mol% of Pd(PPh₃)₄ under benzene reflux for 5 h (Entry 1), 1a successfully underwent

Table 1	The Pd-catalyzed	decarbonylation	of 14
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A Stol-p C O		_cat. Pd(PPh ₃) ₄ ►			c stol-p 8	
Entry	1	A	С	Time/h	8	Yield $(\%)^b$
1	1b	Ph	Н	5	8b	0
2	1a	Ph	p-tolS	1	8a	98
3	1c	$n - C_6 H_{13}$	<i>p</i> -tolS	3	8c	95
4	1d	p-tolS	n-C ₆ H ₁₃	3	8d	6
a 1 (0.5)	mmo	l) and Pd(P	Ph ₃) ₄ (5 mo	1%) under	C_6H_6	(0.5 mL) reflux.

Isolated yield

of 9 ^{<i>a</i>}

	Ar Sto	cat. Pd	(PPh ₃) ₄ ►	ArStol-/ 10	D	
Entry	9	Ar	10	Yield	(%) ^b	
1	9a	Ph	10a	10		
2	9b	o-PhSC ₆ H ₄	10b	97		
3	9c	p-PhSC ₆ H ₄	10c	10		
4	9d	o-ClC ₆ H ₄	10d	71		
5	9e	$p-ClC_6H_4$	10e	13		
6	9f	o-MeOC ₆ H ₄	10f	92		
7	9g	p-MeOC ₆ H ₄	10g	3		
^{<i>a</i>} 9 (0.5 reflux fo	mmol) an	d $Pd(PPh_3)_4$ (5	mol%) under	toluene	(0.5	mL)

decarbonylation to produce the corresponding vinylsulfide 8a in 98% yield after 1 h (Entry 2). Similar results were also obtained when $n-C_6H_{13}$ 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 = Stol-p, C = $n-C_6H_{13}$), the stereoisomer of 1c, was employed as a substrate (6%) of 8d) (Entry 4). Moreover, the generality of the present principle was validated using decarbonvlation of arylthioester ArC(O)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 (Ar = Ph) and 9c (Ar = p-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 β -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 Pd(0)complex took place to form 11, the lone pair in C(C = SAr, Cl, 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 β -*cis* position in α , β -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,¹⁶ 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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reflections measured, 8619 unique, $R(I > 2.0\sigma(I)) = 0.059$, and $R_w(all reflections) = 0.172$. It is possible that methyl H atoms of two C₆H₄Me-*p* groups are incorrectly oriented.

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- 12 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 β -*cis*-SAr coordination site with the C–S bond gradually cleaved.
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