

Catalytic synthesis of thiobutyrolactones via CO insertion into the C–S bond of thietanes in the presence of a heterodinuclear organoplatinum–cobalt complex

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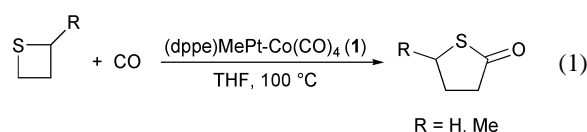
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Heterodinuclear organoplatinum–cobalt complex having a 1,2-bis(diphenylphosphino)ethane ligand (dppe)MePt–Co(CO)₄ catalyzes CO insertion into the C–S bond of thietanes in THF at 100 °C under 1.0 MPa of CO for 2 h to give γ -thiobutyrolactone in quantitative yield.

The cooperative effect of transition metals both in homo- and heterogeneous catalyses is one of the most intriguing unsolved subjects.¹ We previously prepared a series of heterodinuclear organometallic complexes having both M–M' and M–C bonds, L_nRM–M'L'_nL''_m (M = Pt, Pd; M' = Mo, W, Co, Fe, Mn, Re; L = cod, dppe, bpy; L', L'' = Cp, CO)² and found significantly accelerated stoichiometric CO insertion reactions into the Pd–C or Pt–C bonds in the Pd–Co or Pt–Co complex (dppe)MeM–Co(CO)₄, giving (dppe)(MeCO)M–Co(CO)₄ (M = Pd, Pt),^{2fj} in which facile alkyl group transfer and CO insertion at Co followed by oxidative addition to the acyl–cobalt bond are involved. We now report the highly efficient catalytic carbonylation of thietanes promoted by organoplatinum–cobalt heterodinuclear complexes giving thiobutyrolactones. The synthesis of such thiolactones by simple carbonylative ring expansion may also provide a useful tool in organic synthesis.³

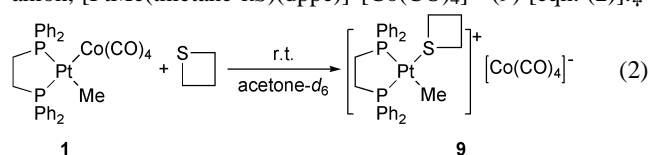
When thietane was heated to 100 °C under 1.0 MPa of CO in THF for 2 h in the presence of 2 mol% of (dppe)MePt–Co(CO)₄ (**1**),^{2c} γ -thiobutyrolactone was selectively formed in quantitative yield (eqn. (1), Table 1, run 1). This carbonylation of thietanes could be achieved quantitatively even at ambient temperature, if the reaction was performed for a day (run 2).



Since the corresponding mononuclear platinum(II) complexes such as PtMeCl(dppe) and [PtMe(MeCN)(dppe)]⁺[BF₄][−] and the anionic cobalt complex [PPN]⁺[Co(CO)₄][−] showed no catalytic activity, the presence of the Pt–Co bond is considered to play an important synergistic

role in this catalytic carbonylation. In contrast, the analogous heterodinuclear Pt–Mn, –Fe, and –Mo complexes (dppe)MePt–ML_n[ML_n = Mn(CO)₅ (**2**),^{2c,h} FeCp(CO)₂ (**3**),^{2c} MoCp(CO)₃ (**4**)^{2c}] and the Pd–Co complex (dppe)MePd–Co(CO)₄ (**5**)^{2fj} showed no or low catalytic activity for the carbonylation of thietane (runs 3–6). Although the catalytic carbonylation of thietane is known to be catalyzed by Co₂(CO)₈ or a mixed metal system Co₂(CO)₈/Ru₃(CO)₁₂, their catalytic activities are less than in our case.⁴ When the ancillary methyl ligand in the heterodinuclear Pt–Co complex was displaced by other organic ligands, a slight change in catalytic activity for this carbonylation was observed. The catalytic activities for neopentyl- and phenylplatinum(II) derivatives [(dppe)RPt–Co(CO)₄]: R = CH₂CMe₃ (**6**), Ph (**7**)[†] decreased to give slightly lower yields than **1** under the same conditions, whereas the acetylplatinum–cobalt complex (dppe)(MeCO)Pt–Co(CO)₄ (**8**)[†] showed comparable catalytic activity to **1** (runs 7–9). When 2-methylthietane⁴ was used as a reactant, γ -thiovalerolactone⁵ was exclusively formed in 89% yield (run 10). The result indicates that insertion of carbon monoxide took place at the less hindered C–S bond of 2-methylthietane, suggesting involvement of an S_N2 type C–S bond cleavage reaction. In fact, carbonylation of 2,5-dimethylthietane⁴ failed under the same reaction conditions.

In order to obtain further mechanistic insights into the present catalytic carbonylation reaction, the stoichiometric reaction of **1** was carried out. When organoplatinum–cobalt complex **1** was treated with thietane in acetone-*d*₆ at room temperature for 1 h, heterolytic cleavage of the Pt–Co bond took place to give a cationic (thietane- κ S)platinum(II) complex with [Co(CO)₄][−] anion, [PtMe(thietane- κ S)(dppe)]⁺[Co(CO)₄][−] (**9**) [eqn. (2)].[‡]



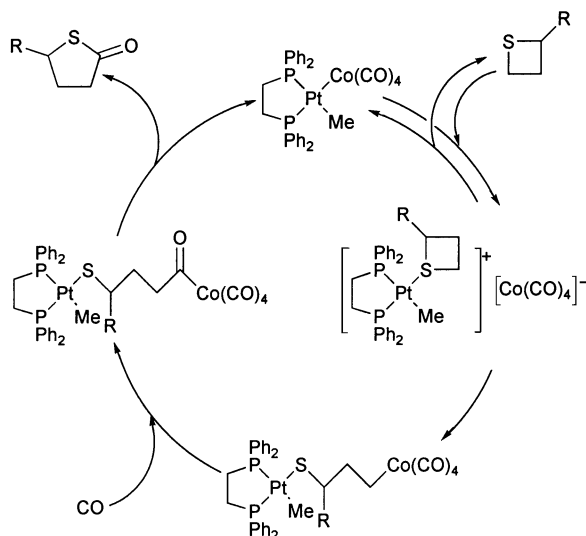
Further treatment of **9** with 0.1 MPa of CO at room temperature afforded a mixture of **1** (71%) and acetylplatinum

Table 1 Catalytic carbonylation of thietane by heterodinuclear organoplatinum–cobalt complexes

Run	R	Catalyst (mol%)	Temperature/ °C	Time/h	Yield(%)
1	H	(dppe)MePt–Co(CO) ₄ (1) (2.0)	100	2	99
2	H	1 (5.0)	30	24	96
3	H	(dppe)MePt–Mn(CO) ₅ (2) (5.0)	100	5	0
4	H	(dppe)MePt–FeCp(CO) ₂ (3) (5.0)	100	5	0
5	H	(dppe)MePt–MoCp(CO) ₃ (4) (5.0)	100	5	8
6	H	(dppe)MePd–Co(CO) ₄ (5) (2.0)	100	2	16
7	H	(dppe)(Me ₃ CCH ₂)Pt–Co(CO) ₄ (6) (2.0)	100	2	60
8	H	(dppe)PhPt–Co(CO) ₄ (7) (2.0)	100	2	84
9	H	(dppe)(MeCO)Pt–Co(CO) ₄ (8) (2.0)	100	2	96
10	Me	1 (2.0)	100	2	89

complex **8** (25%) with concomitant formation of γ -thiobutyrolactone in 91% yield in 2 days.

A plausible mechanism of this catalytic reaction is proposed as shown in Scheme 1.



Scheme 1

The first step of the catalytic cycle is coordination of thietane to Pt to induce heterolytic cleavage of the Pt–Co bond, giving $[\text{PtMe}(\text{thietane-}\kappa\text{S})(\text{dppe})]^+[\text{Co}(\text{CO})_4]^-$. Then the $[\text{Co}(\text{CO})_4]^-$ anion attacks the less-substituted α -S carbon of the coordinated thietane to cause C–S bond cleavage giving the dinuclear complex $(\text{dppe})\text{MePt-SCHR}(\text{CH}_2)_2\text{-Co}(\text{CO})_4$. The formation of such ring-opened products has been shown for the analogous reactions of heterodinuclear complexes $(\text{dppe})\text{RPt-M}(\text{CO})_5$ ($\text{M} = \text{Mn}, \text{Re}$) with three-membered heterocycles such as thiiranes.^{2h} A facile insertion of CO into the cobalt–carbon bond followed by C–S bond formation results in the formation of γ -thiobutyrolactone and regeneration of the starting Pt–Co heterodinuclear complex to close the catalytic cycle.

In conclusion, organoplatinum–cobalt heterodinuclear complexes are shown to catalyze the efficient carbonylation of thietanes under mild conditions. This high catalytic activity is considered to be caused by the presence of a platinum–cobalt bond. Elucidation of the origin of this cooperative effect is under investigation.

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materials” in Tokyo University of Agriculture and Technology.

Notes and references

† Heterodinuclear Pt–Co complexes, $(\text{dppe})\text{RPt-Co}(\text{CO})_4$ [$\text{R} = \text{CH}_2\text{CMe}_3$ (**6**); Ph (**7**)] were prepared in good yields by simple metathesis reactions of $\text{PtR}(\text{NO}_3)(\text{dppe})$ [$\text{R} = \text{CH}_2\text{C}(\text{Me})_3, \text{Ph}$] with sodium tetracarbonylcobaltate $\text{Na}[\text{Co}(\text{CO})_4]$.^{2c} **6**: Yield 87%, mp 155–157 °C (dec.). Anal. Calcd. for $\text{C}_{35}\text{H}_{35}\text{CoO}_4\text{P}_2\text{Pt}$: C, 50.31; H, 4.22. Found: C, 49.98; H, 4.28%. IR (KBr, cm^{-1}): 2020, 1934, 1900, 1847 (νCO). ^1H NMR (acetone- d_6 , rt, 300.4 MHz): δ 0.65 (s, CH_2CMe_3), 2.10 (br, $^2J_{\text{PH}} = 64$ Hz, CH_2Me_3), 2.3–2.7 (m, dppe CH_2), 7.5–7.9 (m, dppe Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6 , rt, 121.6 MHz): δ 42.0 (s, $^1J_{\text{PtP}} = 3999$ Hz, P trans to Co), 47.8 (s, $^1J_{\text{PtP}} = 1521$ Hz, P trans to CH_2CMe_3). **7**: Yield 85%, mp 193–198 °C (dec.). Anal. Calcd. for $\text{C}_{36}\text{H}_{29}\text{CoO}_4\text{P}_2\text{Pt}$: C, 51.38; H, 3.47. Found: C, 51.74; H, 3.67%. IR (KBr, cm^{-1}): 2027, 1954, 1927, 1886 (νCO). ^1H NMR (acetone- d_6 , rt, 300.4 MHz): δ 2.3–2.7 (m, dppe CH_2), 6.53 (t, $^3J_{\text{HH}} = 7.2$ Hz, p -H of Ph), 6.66 (dt, $^3J_{\text{PH}} = 1.6$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, m -H of Ph), 7.02 (t, $^4J_{\text{PH}} = ^3J_{\text{HH}} = 7.2$ Hz, $^3J_{\text{PH}} = 37$ Hz, o -H of Ph), 7.4–7.9 (m, dppe Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6 , rt, 121.6 MHz): δ 42.0 (d, $^2J_{\text{PP}} = 2$ Hz, $^1J_{\text{PtP}} = 3809$ Hz, P trans to Co), 47.8 (d, $^2J_{\text{PP}} = 2$ Hz, $^1J_{\text{PtP}} = 1661$ Hz, P trans to Ph). $(\text{dppe})(\text{MeCO})\text{Pt-Co}(\text{CO})_4$ (**8**)^{2f,j} was synthesized by the oxidative addition of $\text{Co}(\text{COMe})(\text{CO})_4$ to $\text{Pt}(\text{styrene})(\text{dppe})$.

‡ Spectroscopic data for **9**: ^1H NMR (acetone- d_6 , rt, 300.4 MHz): δ 0.46 (dd, $^3J_{\text{PH}} = 3.9, 6.0$ Hz, $^2J_{\text{PH}} = 56.8$ Hz, Pt–Me), 2.4–2.7 (m, dppe CH_2), 3.0–3.4 (br, SCH_2CH_2), 3.5–3.8 (br, SCH_2), 7.4–7.9 (m, dppe Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6 , rt, 121.6 MHz): δ 42.9 (d, $^2J_{\text{PP}} = 2$ Hz, $^1J_{\text{PtP}} = 3510$ Hz, P trans to S), 47.8 (d, $^2J_{\text{PP}} = 2$ Hz, $^1J_{\text{PtP}} = 1820$ Hz, P trans to Ph).

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