Preparation, crystal structures and isomerization kinetics of *cis*- and *trans*-[Co(dtc)₂(PHPh₂)₂]⁺: thermodynamically and kinetically stable cobalt(III)–P bonds through interplay of σ-donicity, π-acidity, and steric bulkiness

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Novel cobalt(III)–diphenylphosphine complexes, *cis*- and *trans*-[Co(dtc)₂(PHPh₂)₂]⁺, were synthesized and structurally characterized by X-ray crystallographic analyses and spectroscopic methods. The Co–P bond lengths in both isomers were shorter than those in the analogous cobalt(III)–bis(tertiary phosphine) complexes with sterically less bulky but more basic phosphine ligands: Co–P(1) = 2.2340(6) and Co–P(2) = 2.2258(7) Å for the *cis*-isomer, and Co–P = 2.276(1) Å for the *trans* isomer. The title complexes also exhibited a unique dynamic behavior: *cis* to *trans* isomerization was induced by irradiation with visible light, while thermal *trans* to *cis* isomerization took place at elevated temperatures. The absorbance change for the *trans* to *cis* isomerization reaction exhibited multi-exponential kinetic traces when no free PHPh₂ was present in the solution. Such a complicated kinetic behavior was explained either by the slow dissociation of coordinated PHPh₂ or by the abstraction of a P–H proton from coordinated PHPh₂ through an acid–base interaction with trace water in the bulk solvent. By addition of an excess amount of PHPh₂, the dissociation of coordinated PHPh₂ as well as the basicity of impure water was suppressed, and a first-order kinetic trace was observed. Kinetic studies with excess free PHPh₂ in acetonitrile revealed that the isomerization reaction takes place *via* an intramolecular twist mechanism: $\Delta H^* = 120 \pm 1$ kJ mol⁻¹ and $\Delta S^* = 50 \pm 18$ J mol⁻¹ K⁻¹. AOM calculations indicate that the twist mechanism involves a spin state change ($^1A_{1g}$ to $^5A_1'$) during the activation process. The importance of the π-acidity of PHPh₂ together with the cooperative effect of the spectator ligand (dtc⁻) was suggested to explain the thermodynamic and kinetic behaviors of these complexes.

Introduction

Stable mononuclear secondary phosphine complexes are excellent candidates for the investigation of agostic M · · · H–P[1] and hydrogen-bonding O · · · H–P[2] interactions. They also provide rational synthetic methods for the heterometallic phosphide-bridged dinuclear complexes through deprotonation of the phosphine ligand. Diphenylphosphine (PHPh₂), a typical secondary phosphine, is believed to be a weak σ-donor ($\chi_d = 17.35$) and is one of the phosphines claimed to possess no π-acidity.[3] Diphenylphosphine also has a strong propensity to produce homometallic diphenylphosphide (Ph₂P⁻)-bridged di- or poly-nuclear species by deprotonation upon coordination. On this basis, relatively few mononuclear transition-metal complexes containing PHPh₂ have been reported,[4–9] compared with a large number of tertiary phosphine complexes.

We have recently succeeded in the preparation and characterization of mixed-ligand dithiocarbamatocobalt(III) complexes with various phosphites [P(OMe)₃, P(OEt)₃, and P(OCH₂)₃-CEt].[10] These phosphite ligands are expected to exhibit similar weak σ-donicity to PHPh₂, while the π-acidity of these phosphites are believed to be high. Moreover, PHPh₂ is sterically more bulky according to Tolman's cone angles compared with these phosphites; PHPh₂, $\theta = 128°$; P(OMe)₃, 107°; P(OEt)₃, 109°; and P(OCH₂)₃CEt, 101°.[11] Therefore, the dithiocarbamatocobalt(III) frame seems to be an excellent candidate for the synthesis of potentially useful PHPh₂ complexes and for the

investigation of the nature of metal–P bonds, as the compact bidentate dithiocarbamate ligand provides less steric hindrance around the metal center. The reported pK_a values for the conjugate cations of P(OMe)₃, P(OEt)₃, and P(OCH₂)₃CEt are 2.60, 3.31, and 1.74, respectively.[3] With this in mind, it seems that proton affinity, and therefore the affinity to the hard cobalt(III) ion, of these phosphites are rather low, and that the high stability of dithiocarbamatocobalt(III) complexes with these phosphites may be attributed to the strong π-back donation. Moreover, the bond strength between cobalt(III) and PHPh₂ should be very weak if PHPh₂ exhibits no π-acidity as indicated by Giering and co-workers,[3] since the pK_a values for the conjugate cation of PHPh₂ is merely 0.03.

To examine the exact nature of metal–P interactions, it is important to know the molecular structure, spectroscopic and chemical properties of the phosphite and/or secondary phosphine complexes.[10] For this purpose, we tried to synthesize PHPh₂ complex of a typical hard cobalt(III) ion.[12] In this study, we report a pair of geometrical isomers of novel cobalt(III) complexes containing PHPh₂ and *N*,*N*-dimethyldithiocarbamate (dtc⁻): *cis*- and *trans*-[Co(dtc)₂(PHPh₂)₂]BF₄.

The thermal isomerization reaction from *trans*- to *cis*-[Co(dtc)₂(PHPh₂)₂]⁺ in acetonitrile was also examined for the clarification of the π-acidity problem with phosphine ligands originally discussed by Giering and co-workers.[3] Especially for d⁶ cobalt(III) complexes with filled t₂g orbitals, an associative attack of the incoming ligand to induce cobalt(III)–P bond dis-

sociation is not likely to occur. Thermal isomerization reactions of such inert octahedral complexes have been known to take place either through the twist mechanism or through dissociation of one of the coordinated ligands.[13] The activation enthalpies for these two processes were evaluated on the basis of the method postulated by Vanquickenborne and Pierloot,[14,15] and compared with the experimentally obtained results.

Experimental

Preparation of the complexes

cis-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$. The *cis*-isomer was prepared as follows in an atmosphere of argon in the dark. To an ethanol solution (30 cm^3) of Co(BF$_4$)$_2$·6H$_2$O (0.68 g, 2.0 mmol) was added PHPh$_2$ (0.92 g, 4.9 mmol), and the mixture was stirred for 1 h at room temperature to give an orange–yellow suspension. The suspension was cooled in an ice bath, and a solution of tetramethylthiuram disulfide (0.48 g, 2.0 mmol) in a mixture of ethanol and dichloromethane (3 : 1, 80 cm^3) was added dropwise with stirring over 2 h. The reaction mixture was stirred for a further 2 h at room temperature. The resulting red precipitate was collected by filtration, washed with diethyl ether (3 × 30 cm^3), and dried *in vacuo* (yield 0.96 g, 63%). Anal. found: C, 47.20; H, 4.49; N, 4.03%. Calc. for C$_{30}$H$_{34}$BCoF$_4$-N$_2$P$_2$S$_4$: C, 47.50; H, 4.52; N, 3.69%. ^{1}H NMR (CD$_2$Cl$_2$, TMS): δ 2.781 (s, 6H, –NCH$_3$), 2.936 (s, 6H, –NCH$_3$), 6.125 (dd, $^1J_{\text{P–H}}$ = 359.3 Hz, $^3J_{\text{P–H}}$ = 30.0 Hz, 2H, P–H), 7.373–7.555 (m, 20H, –C$_6$H$_5$). ^{31}P{^{1}H} NMR (85% H$_3$PO$_4$): δ 33.7. ^{59}Co{^{1}H} NMR (K$_3$[Co(CN)$_6$]): δ 2697. Single-crystals suitable for X-ray diffraction study were obtained by diffusion of diethyl ether vapor into the acetonitrile solution.

trans-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$. The *trans*-isomer was prepared by a photochemical reaction from the *cis*-isomer in a nearly quantitative yield. A solution of *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$ in a mixture of methanol and acetonitrile (1 : 1) was evaporated in the open air under exposure to room light (fluorescent 15 W desk lamp) over 3 days. Dark red columnar crystals of the *trans*-isomer were deposited almost quantitatively. Anal. found: C, 47.09; H, 4.41; N, 3.79%. Calc. for C$_{30}$H$_{34}$BCoF$_4$N$_2$P$_2$S$_4$: C, 47.50; H, 4.52; N, 3.69%. ^{1}H NMR (CD$_2$Cl$_2$, TMS): δ 2.585 (s, 12H, –NCH$_3$), 6.625 (dd, $^1J_{\text{P–H}}$ = 263.6 Hz, $^3J_{\text{P–H}}$ = 119.8 Hz, 2H, P–H), 6.984–7.356 (m, 8H, –C$_6$H$_5$), 7.417–7.455 (m, 4H, –C$_6$H$_5$), 7.626–7.667 (m, 8H, –C$_6$H$_5$). ^{31}P{^{1}H} NMR (85% H$_3$PO$_4$): δ 27.3. ^{59}Co{^{1}H} NMR (K$_3$[Co(CN)$_6$]): δ 3224.

The *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ complex was also prepared by the substitution of triphenylphosphine in *trans*-[Co(dtc)$_2$-(PPh$_3$)$_2$]$^+$ for PHPh$_2$. A suspension of *trans*-[Co(dtc)$_2$(PPh$_3$)$_2$]-BF$_4$[16] (1.4 g, 1.5 mmol) in methanol (80 cm^3) was cooled in an ice bath, and a methanol solution (30 cm^3) of PHPh$_2$ (0.72 g, 3.9 mmol) was added dropwise with stirring over 20 min. The reaction mixture was stirred for 1 d at room temperature and the resulting yellow brown precipitate was filtered, recrystallized by dissolving in methanol–dichloromethane (2 : 1) and slow evaporation of dichloromethane. Dark red crystals of *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$ were obtained (yield 0.68 g, 58%). The results of the elemental analysis as well as the ^{1}H NMR signals of this compound indicate that the product prepared by this procedure is identical to that prepared by the photochemical method.

Measurements

The NMR spectra were obtained in dichloromethane-d_2 at 30 °C by a JEOL Lambda 500 spectrometer. UV-Vis absorption spectra in CH$_2$Cl$_2$ were measured by a Perkin-Elmer Lambda 19 spectrophotometer at room temperature. For the kinetic measurements in acetonitrile-d_3, a Bruker AMX400WB spectrometer was used at controlled temperatures. Kinetic

measurements of the isomerization reactions were also monitored under an argon atmosphere on JASCO V-560, V-570, and Shimadzu UV-1600 spectrophotometers. The temperature of all sample solutions was held constant within ± 0.2 K. Acetonitrile used for the kinetic measurements was obtained from Wako Pure Chemicals Inc., and purified by distillation from phosphorus pentoxide. The amount of residual water in thus purified acetonitrile was examined using a Mitsubishi Kasei CA01 Karl-Fisher apparatus, by which it was determined to *ca.* 1 mmol kg^{-1}. Trace amounts of water (*ca.* < 10 mmol kg^{-1}) introduced into the sample solutions during preparation is mentioned as "impure water" throughout this article, otherwise the solvent is very pure.

Tetra-*n*-butylammonium tetrafluoroborate (0.1 mol kg^{-1}) was used to adjust the ionic strength. All sample solutions were prepared under an inert atmosphere. Electrochemical measurements were carried out using a BAS 100B Electrochemical Analyzer at 20 °C. A platinum disk was used as the working electrode. A Pt wire was used as the counter electrode, while Ag/AgNO$_3$ in acetonitrile was used as the reference electrode. The redox potentials of sample solutions were calibrated using the ferricinium/ferrocene redox signal. Tetra-*n*-butylammonium perchlorate (0.1 mol kg^{-1}) was used as the supporting electrolyte.

Crystal structure determination

For the *trans*-isomer, the X-ray intensities were measured on an automated Rigaku four-circle diffractometer AFC-5R [23 °C, graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), the 2θ–ω scan mode, $2\theta_{\text{max}}$ = 60°, three standard reflections monitored every 150 reflections with no serious decomposition]. The intensities of the *cis*-isomer were measured on a Rigaku imaging plate area detector Raxis-rapid [20 °C, graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), the oscillation scan mode, $2\theta_{\text{max}}$ = 55°, 100 × 100 pixel mode]. The structures were solved by direct methods using the SHELXS86 program,[17] and refined using the SHELXL97 program[18] (on F^2, full-matrix, complex neutral-atom scattering factors, and anisotropic thermal parameters for all non-H atoms). The H atoms bound directly to the P atoms were located at the position obtained by the D-syntheses map and refined isotropically, and all the other H atoms were introduced at the theoretical positions with the riding model.

Crystal data for *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$·CH$_3$CN·0.5Et$_2$O. FW = 836.63, dark red block, 0.48 × 0.42 × 0.30 mm, monoclinic, P2/n (no. 13), a = 19.359(1), b = 11.1101(7), c = 20.642(1) Å, β = 115.830(2)°, U = 2996.3(4) Å^3, Z = 4, D_{calc} = 1.391 Mg m^{-3}, $F(000)$ = 1732, μ = 0.767 mm^{-1}, 9084 independent reflections, 6901 reflections having $F^2 > 2\sigma(F^2)$, R1 [F^2: $F^2 > 2\sigma(F^2)$] = 0.040, wR2 (F^2: all reflections) = 0.117.

Crystal data for *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$. FW = 758.51, dark red column, 0.40 × 0.20 × 0.10 mm, monoclinic, C2/c (no. 15), a = 19.507(4), b = 14.529(5), c = 14.445(3) Å, β = 122.20(1)°, U = 3464(1) Å^3, Z = 4, D_{calc} = 1.454 Mg m^{-3}, $F(000)$ = 1560, μ = 0.875 mm^{-1}, 5070 independent reflections, 2841 reflections having $F^2 > 2\sigma(F^2)$, R1 [F^2: $F^2 > 2\sigma(F^2)$] = 0.055, wR2 (F^2: all reflections) = 0.147.

CCDC reference numbers 172897 and 172898.

See http://www.rsc.org/suppdata/dt/b2/b203792k/ for crystallographic data in CIF or other electronic format.

Results and discussion

Preparation and characterization of the complexes

A reaction of the orange suspension of Co(BF$_4$)$_2$·6H$_2$O (2.0 mmol) and PHPh$_2$ (4.9 mmol) in ethanol (30 cm^3) with tetramethylthiuram disulfide (2.0 mmol) solution in ethanol–

dichloromethane (3 : 1, 80 cm³) in the dark gave red precipitates with the composition [Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$. The ^{1}H NMR of the product in dichloromethane-d_2 exhibited a spectrum corresponding to the structure of cis-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$: two singlet resonances at δ 2.781 and 2.936 for N–CH$_3$. The P–H resonance was observed at δ 6.125 with $^1J_{P-H}$ = 359.3 and $^3J_{P-H}$ = 30.0 Hz. Recrystallization from acetonitrile–diethyl ether in the dark gave red crystals suitable for single-crystal X-ray structure analysis, which confirmed the molecular structure of the cis-isomer.

When the solution of cis-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$ in dichloromethane, acetonitrile, or methanol was placed under a fluorescent 15 W desk lamp for several days, the complex isomerized to the corresponding trans-isomer almost quantitatively. The crystals of trans-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$ were deposited by evaporation of the solution in the open air. The ^{1}H NMR spectrum of the trans-isomer in dichloromethane-d_2 exhibited a singlet resonance at δ 2.585 for N–CH$_3$, and the P–H resonance at δ 6.625 with $^1J_{P-H}$ = 263.6 and $^3J_{P-H}$ = 119.8 Hz. The molecular structure was also confirmed by single-crystal X-ray analysis (vide infra). The trans-isomer was thermally reconverted to the original cis-isomer, when the solution was heated in the dark.

The trans-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ complex was also prepared by the chemical reaction of trans-[Co(dtc)$_2$(PPh$_3$)$_2$]BF$_4$ with PHPh$_2$ in alcoholic media. Such a synthetic route to convert trans-bis(triphenylphosphine) complex to trans-isomers with less bulky phosphine ligands by the ligand substitution reaction may also be applied to the syntheses of a series of trans-[Co(dtc)$_2$(P-ligand)$_2$]$^+$ complexes.[19]

The ^{1}H NMR spectra of these complexes in dry acetonitrile-d_3 were similar to those in dichloromethane-d_2. However, the P–H proton signals of free PHPh$_2$ significantly broadened by the addition of a small amount of water to the acetonitrile-d_3 solution of PHPh$_2$, while no significant change in the P–H signals was observed for the coordinated PHPh$_2$ on trans- and cis-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ complexes by addition of water. Therefore, the acid–base interaction of the P–H proton with impure water is significant for PHPh$_2$ in the bulk, while such an interaction can be ignored for the coordinated PHPh$_2$, indicating that π-back donation to PHPh$_2$ enhances electron density on the coordinated P atom. On the other hand, in methanol-d_4, which contains a small amount of water as an impurity, the P–H resonances of coordinated PHPh$_2$ completely disappeared 3 days after sampling at 298 K, while the other resonance signals corresponding to N–CH$_3$ and phenyl groups were observed at identical positions to those observed in acetonitrile-d_3 and dichloromethane-d_2. It should be noted, however, that the P–H proton signals of coordinated PHPh$_2$ were not broadened in freshly prepared solutions of methanol-d_4. These observations indicate that the coordinated PHPh$_2$ gradually releases its P–H proton in methanol, while the addition of free PHPh$_2$ suppressed the abstraction of P–H from coordinated PHPh$_2$. (see Appendix 1).

No ^{1}H NMR signal of free PHPh$_2$ was observed even for the sealed acetonitrile-d_3 solution that contained 0.01 mol kg^{-1} of trans- or cis-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ with water contents of much less than 1 mmol kg^{-1} (the amount of water was under the detection limit of the Karl-Fisher apparatus). Therefore, it is indicated that trans- and cis-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ are inert, but gradually release the P–H proton from coordinated PHPh$_2$ in methanol and probably also in acetonitrile when no free PHPh$_2$ is added to the solution.

Crystal structures

Single-crystal X-ray analyses have revealed the geometrical structures of the complexes. The molecular structures of the complex cations in cis-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$·CH$_3$CN·0.5Et$_2$O and trans-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$ are shown in Fig. 1. The P–H bond lengths are 1.21(3) Å for the trans-isomer, and 1.37(3) and
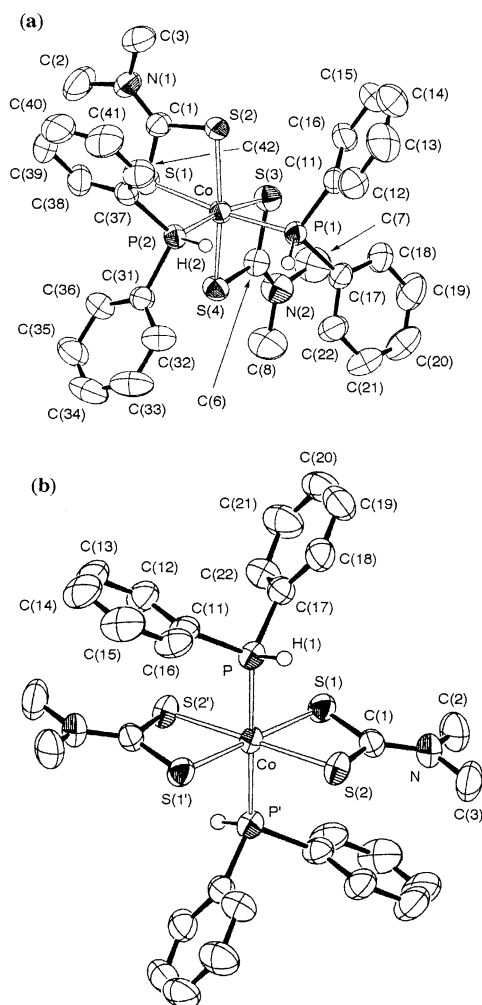

Fig. 1 (a) Perspective drawing (50% probability level) of the cationic part of cis-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$·CH$_3$CN·0.5Et$_2$O and (b) perspective drawing (50% probability level) of the cationic part of trans-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$. Hydrogen atoms, except for those directly bound to P atoms, are omitted for clarity.

1.36(2) Å for the cis-isomer, which is consistent with the observation that the $^1J_{P-H}$ of the ^{1}H NMR signal is significantly reduced for the trans-isomer.

In the structure of the cis-isomer, two phenyl rings of PHPh$_2$ are oriented in a way that the intramolecular steric interaction between two PHPh$_2$ ligands is minimized (Fig. 1a). Stacking interactions between a dtc plane and one of the phenyl rings are observed for each PHPh$_2$. The Co–P(1) and Co–P(2) bond lengths are 2.2340(6) and 2.2258(7) Å, respectively, which are shorter than those in cis-[Co(dtc)$_2$(PMe$_2$Ph)$_2$]PF$_6$ with sterically less bulky but more basic PMe$_2$Ph (cone angle θ = 122° and $χ_d$ = 10.60): Co–P(1) and Co–P(2) are 2.2795(6) and 2.2637(7) Å, respectively.[19] The P(1)–Co–P(2) angle is 90.51(2)°, which is remarkably smaller than the other cis-[Co(dtc)$_2$(P-ligand)$_2$]$^+$ type complexes.[10,19] There is apparently no reasonable relationship between these structural parameters (Co–P lengths and P–Co–P angles) and either the Tolman's cone angle or σ-donicity of these P-ligands.

The Co–S bond lengths and the bite angles of dtc in trans-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ are comparable to those in the series of complexes, trans-[Co(dtc)$_2$(PMe$_{3-n}$Ph$_n$)$_2$]BF$_4$ (n = 1, 2 and 3) (Fig. 1b).[19] The Co–P bond lengths of trans-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ [2.276(1) Å] are shorter than those of trans-[Co(dtc)$_2$(PMe$_{3-n}$Ph$_n$)$_2$]BF$_4$, although PMe$_2$Ph and PMe$_3$ are sterically smaller and stronger σ-donors compared with PHPh$_2$. Since Co–P bond lengths are usually related to the electronic trans influence of phosphines, the short Co–P bond lengths in

Table 1 Gaussian curve fitting results for absorption spectra of the complexes, 10^{-3} σ/cm^{-1} ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$)[a]

Complex	d–d band		CT-band		
cis-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$	18.43 (653.9)	23.43 (2611)	27.88 (5354)	31.17 (7791)	34.59 (26770)
cis-[Co(dtc)$_2$(PMe$_3$)$_2$]BF$_4$	18.33 (740.8)	23.31 (1340)	29.25 (10560)	32.62 (24990)	
cis-[Co(dtc)$_2$(PMe$_2$Ph)$_2$]PF$_6$	17.91 (742.6)	22.96 (1716)	28.89 (15200)	32.04 (21800)	
cis-[Co(dtc)$_2${P(OMe)$_3$}$_2$]BF$_4$	19.41 (704.2)	23.73 (1552)	29.03 (9840)	34.08 (26980)	
trans-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$	17.30 (369.0)	21.12 (616.5)[b]	24.92 (10910)	29.63 (21130)	
trans-[Co(dtc)$_2$(PMe$_3$)$_2$]BF$_4$	17.90 (258.1)	22.81 (587.0)[b]	27.38 (13540)	30.11 (21970)	
trans-[Co(dtc)$_2$(PMe$_2$Ph)$_2$]BF$_4$	17.17 (225.4)	22.12 (665.8)[b]	25.57 (12090)	29.70 (25120)	
trans-[Co(dtc)$_2$(PMePh$_2$)$_2$]BF$_4$	16.58 (354.5)	19.97 (546.9)	24.77 (10950)	29.63 (21750)	
trans-[Co(dtc)$_2$(PPh$_3$)$_2$]BF$_4$	15.74 (342.3)	20.20 (868.7)[b]	23.08 (9488)	30.18 (22290)	
[Co(dtc)$_3$]	15.50 (435.2)	20.62 (588.9)	25.87 (8437)	27.73 (2794)	31.21 (19490)

[a] In CH$_2$Cl$_2$ at room temperature. [b] Very broad shoulder in the observed spectra.

the PHPh$_2$ complexes may reflect the relatively weak nature of the *trans* interaction (influence).

Absorption spectra

The UV-vis absorption spectrum of cis-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$ in CH$_2$Cl$_2$ is very similar to those of cis-[Co(dtc)$_2$(PMe$_3$)$_2$]BF$_4$ and cis-[Co(dtc)$_2${P(OMe)Ph$_2$}$_2$]PF$_6$ [20] in the region up to 33000 cm^{-1} (Fig. 2a). There are two d–d bands around 18500 and

Fig. 2 legend (a):
— cis-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$ / CH$_2$Cl$_2$ (r.t.)
- - - cis-[Co(dtc)$_2${P(OMe)Ph$_2$}$_2$]PF$_6$ / CH$_2$Cl$_2$ (r.t.)
-·-· cis-[Co(dtc)$_2$(PMe$_3$)$_2$]BF$_4$ / CH$_2$Cl$_2$ (r.t.)

Fig. 2 legend (b):
— trans-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$ / CH$_2$Cl$_2$ (r.t.)
- - - trans-[Co(dtc)$_2$(PMePh$_2$)$_2$]PF$_6$ / CH$_2$Cl$_2$ (r.t.)
-·-· trans-[Co(dtc)$_2$(PPh$_3$)$_2$]PF$_6$ / CH$_2$Cl$_2$ (r.t.)
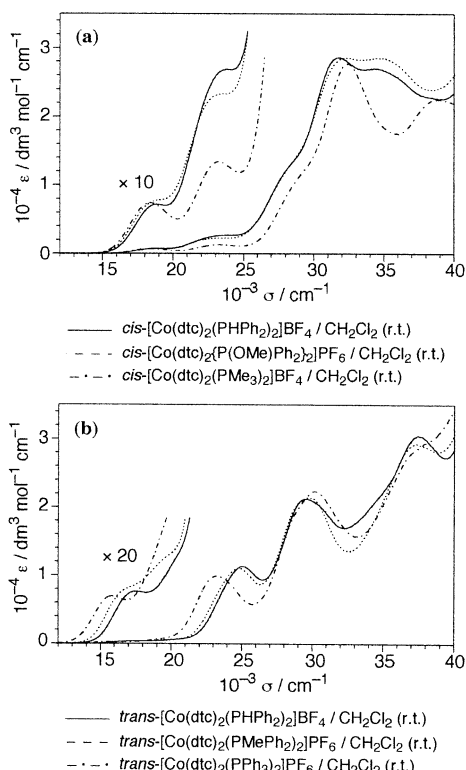
Fig. 2 Absorption spectra of (a) *cis*- and (b) *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ and related complexes in dichloromethane.
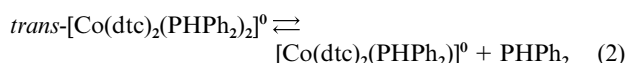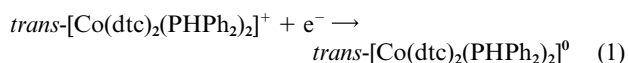
23300 cm^{-1}, although the intensity of the second d–d band of the PHPh$_2$ and P(OMe)Ph$_2$ complexes is about twice as much as that of the PMe$_3$ complex. The Gaussian curve analyses gave the energies of these two bands as: σ/cm^{-1} ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 18430 (654) and 23430 (2611), 19410 (704) and 23730 (1552), 18330 (741) and 23310 (1340) for the PHPh$_2$, P(OMe)$_3$, and PMe$_3$ complexes, respectively (Table 1). The ligand-field strength, Δ, and Racah's inter-electronic repulsion parameter, B, were calculated as 19680 and 313, 20490 and 270, 19570 and 311 cm^{-1} for the PHPh$_2$, P(OMe)$_3$, and PMe$_3$ complexes, respectively. The relatively large Δ value for the PHPh$_2$ complex indicates that the ligand-field by PHPh$_2$ is not small compared with the stronger σ-donor, PMe$_3$. Moreover, the relatively small value of B for PHPh$_2$ strongly indicates that inter-electronic

repulsion between the d-electrons on cobalt(III) is significantly reduced by the coordination of PHPh$_2$. Therefore, although the σ-donicity is small for PHPh$_2$, it seems that the relatively large π-acidity of PHPh$_2$ induces a large ligand-field and reduces inter-electronic repulsion. If the PHPh$_2$ ligand exhibits no π-acidity, as suggested by Geiring and co-workers,[3] the observed large Δ value and small B value for PHPh$_2$ may not be rationally explained. However, the electronic effect of the spectator ligands such as dtc$^-$ may also participate in the enhancement of the apparent ligand-field.

The absorption spectrum of trans-[Co(dtc)$_2$(PHPh$_2$)$_2$]BF$_4$ exhibited the $^1_aE_g$ component of the first d–d transition at 17300 cm^{-1} (ε = 369 dm^3 mol^{-1} cm^{-1}) and the lowest energy LMCT band at 24920 cm^{-1} (ε = 10910 dm^3 mol^{-1} cm^{-1}) (Fig. 2b). The corresponding bands for trans-[Co(dtc)$_2$(PMePh$_2$ or PPh$_3$)$_2$]BF$_4$ were observed at 16580 and 24770 cm^{-1} for PMePh$_2$ and 15740 and 23080 cm^{-1} for the PPh$_3$ complexes, respectively. Since σ-donicity of the phosphine ligands decreases in the order of PMePh$_2$ (χ_d = 12.10) > PPh$_3$ (13.25) > PHPh$_2$ (17.35), the ligand-field strengths do not directly relate to the σ-donicity of these ligands. Again, π-acidity of these ligands has to be taken into account. However, the effect of the steric bulk of these phosphine ligands may also play a significant role in determining the order of Δ and B values: PHPh$_2$ (θ = 128°) < PMePh$_2$ (136) < PPh$_3$ (145).

Electrochemical studies of *trans*- and *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ in acetonitrile

Cyclic voltammograms of *trans*- and *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ ions at 20 °C are shown in Fig. 3. Tetra-*n*-butylammonium perchlorate (0.1 mol kg^{-1}) was used as supporting electrolyte. As seen in Fig. 3a, an irreversible signal was observed for *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ in the −0.85 to −1.05 V region *vs.* ferricinium/ferrocene couple. With the existence of excess free PHPh$_2$, the cathodic signal corresponding to the [Co(dtc)$_2$(PHPh$_2$)$_2$]$^{+/0}$ couple moved toward more negative potential and a clear anodic signal appeared as shown in Fig. 3a, indicating the electrode process involves the following EC mechanism.[21,22]

$$trans\text{-}[Co(dtc)_2(PHPh_2)_2]^+ + e^- \longrightarrow$$
$$trans\text{-}[Co(dtc)_2(PHPh_2)_2]^0 \quad (1)$$

$$trans\text{-}[Co(dtc)_2(PHPh_2)_2]^0 \rightleftharpoons$$
$$[Co(dtc)_2(PHPh_2)]^0 + PHPh_2 \quad (2)$$

Addition of excess free PHPh$_2$ suppresses reaction (2) and the voltammogram became reversible as shown in Fig. 3a. From the ratio of the anodic and cathodic peak currents of the voltammogram for the solution without free PHPh$_2$, the dissociation rate constant of PHPh$_2$ from *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]^0 was estimated as 0.2 s^{-1} at 20 °C by using the numerical working curve reported elsewhere.[21,22]

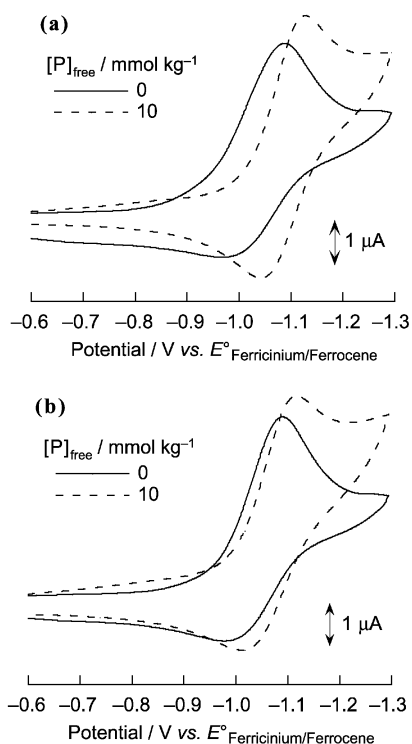The voltammograms of *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ in acetonitrile with and without free PHPh$_2$ were similar to those

(a)

$[P]_{free}$ / mmol kg^{-1}
—— 0
- - - - - 10

1 μA

−0.6 −0.7 −0.8 −0.9 −1.0 −1.1 −1.2 −1.3

Potential / V *vs.* $E°_{Ferricinium/Ferrocene}$

(b)

$[P]_{free}$ / mmol kg^{-1}
—— 0
- - - - - 10

1 μA

−0.6 −0.7 −0.8 −0.9 −1.0 −1.1 −1.2 −1.3

Potential / V *vs.* $E°_{Ferricinium/Ferrocene}$

Fig. 3 Cyclic voltammograms of (a) *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ and (b) *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ at 293 K in acetonitrile. [Co(dtc)$_2$(PHPh$_2$)$_2^+$] = 1.0 mmol kg^{-1}. Tetra-*n*-butylammonium perchlorate (0.1 mol kg^{-1}) was used as the supporting electrolyte. Scan rate = 100 mV s^{-1}.

observed for the *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^{+/0}$ couple (Fig. 3b). Therefore, a similar EC mechanism as described by reactions (1) and (2) is also applicable to this redox couple, and the dissociation rate constant of PHPh$_2$ from *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]^0 was determined as 0.1 s^{-1} from the peak current ratios. The limiting $E_{1/2}$ values with excess free PHPh$_2$ for the *trans*- and *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^{+/0}$ couples were identical to each other, −1.16 V *vs.* ferricinium/ferrocene couple. Therefore, the LUMO level, presumably the e$_g$ level, of these cobalt(III) species are similar to each other in acetonitrile.

As the solvent exchange rate constant for high-spin solvated cobalt(II) in solution is of the order of 10^6 s^{-1} at 298 K,[13] the rather small dissociation rate constants obtained from the electrochemical measurements, 0.2 and 0.1 s^{-1} for *trans*- and *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]^0, respectively, indicates that these Co(II) species may be in the low-spin state and the Co(II)–P bonds are rather strong.

Kinetic measurements

NMR studies. Prior to the spectrophotometric measurements, two independent sets of experiments were carried out to examine the salt effect on the isomerization reaction by using a Bruker AMX-400 WB NMR (the sample solutions were sealed by using a vacuum line): (1) ^{1}H–NMR signal (area) change of 0.01 mol kg^{-1} solutions of *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ with and without 0.1 mol kg^{-1} CF$_3$SO$_3$Na in acetonitrile-d_3 at 333 and 298 K, and (2) the effect of different supporting electrolytes (tetra-*n*-butylammonium perchlorate, tetra-*n*-butylammonium trifluoromethanesulfonate, and CF$_3$SO$_3$Na) on the rate of *trans* to *cis* isomerization were examined. The sample solutions were maintained at each set temperature, and the change in the area corresponding to the N–CH$_3$ proton signals was monitored. One of the results is shown in Fig. 4.
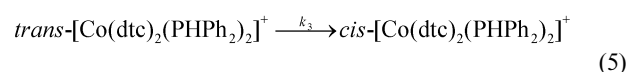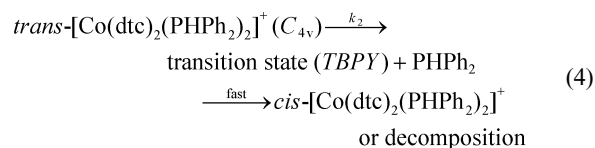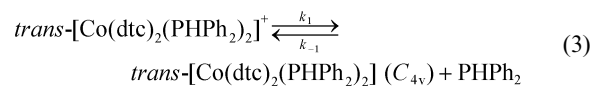
No significant degree of isomerization was observed for all tested samples at 298 K for several hours. The area ratio of P–H proton and N–CH$_3$ protons was always 1 : 6 for all samples, indicating that the structures of *cis*- and *trans*-

[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ in the crystal are retained in solution within the sensitivity limit of the NMR measurement. The isomerization rate constant estimated from the increase in area of the N–CH$_3$ signals of the *cis*-isomer (Fig. 4) was 4.0 × 10^{-4} s^{-1} at 333 K. This value is consistent with that obtained by the spectrophotometric method with excess amounts of free PHPh$_2$ in the bulk, 4.3 × 10^{-4} s^{-1} (see next section). Moreover, no appreciable dependence of the *trans* to *cis* conversion rate on the type of the salt was observed. As no appreciable influence of different types of anion or cation on the rate of the reaction was observed, tetra-*n*-butylammonium tetrafluoroborate was used to adjust the ionic strength of the sample solutions in the following spectrophotometric measurements.

Spectrophotometric studies. The isomerization reaction in acetonitrile was observed by monitoring the increase of the absorption of the *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ at 540 nm (Fig. 5).

As noted in the section on NMR measurements, the gradual disappearance of the P–H proton signals correspond to either a slow dissociation of P–H proton from coordinated PHPh$_2$ or dissociation of PHPh$_2$ in acetonitrile and methanol that contain small amounts of water (< 5 mmol kg^{-1}). Contamination of the solvents with a trace amount of water (< 5 mmol kg^{-1}) was unavoidable during the sampling process for the spectrophotometric measurements. As a result, multi-exponential kinetic traces were observed in acetonitrile that contained no free PHPh$_2$ in the bulk. On the other hand, the absorption changes corresponding to the isomerization reaction followed exact first-order kinetics with excess amounts of free PHPh$_2$, $[PHPh_2]_{free}$ > 15 mmol kg^{-1}. It should also be noted that the spectral change even of the sample solutions without free PHPh$_2$ exhibited identical isosbestic points to those observed for the solutions containing sufficient amounts of free PHPh$_2$ (Fig. 5). We believe that either a very small amount of coordinated PHPh$_2$ dissociates from *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ or *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ releases its P–H proton. In both cases, the succeeding slower isomerization process causes the observed multi-exponential kinetic behavior shown in Fig. 5 (see Appendix 2). The total amount of water was determined to be less than 5 mmol kg^{-1} for all sample solutions used for the spectrophotometric measurements. Therefore, by the addition of excess amounts of free PHPh$_2$, it is expected that both dissociation of PHPh$_2$ from *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ and dissociation of the P–H proton from coordinated PHPh$_2$ may be suppressed.

The reactions were excellently first-order up to three half-lives for each reaction, when more than 15 mmol kg^{-1} of free PHPh$_2$ was added to the solutions. The results are summarized in Table 2. The apparent isomerization rate constant, k_{obs}, should depend on the concentration of free PHPh$_2$ if the reaction involves an appreciable contribution from the dissociation mechanism:

$$trans\text{-[Co(dtc)}_2(PHPh_2)_2]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$
$$trans\text{-[Co(dtc)}_2(PHPh_2)_2]\ (C_{4v}) + PHPh_2 \quad (3)$$

$$trans\text{-[Co(dtc)}_2(PHPh_2)_2]^+\ (C_{4v}) \xrightarrow{k_2}$$
$$\text{transition state } (TBPY) + PHPh_2$$
$$\xrightarrow{fast} cis\text{-[Co(dtc)}_2(PHPh_2)_2]^+ \quad (4)$$
$$\text{or decomposition}$$

$$trans\text{-[Co(dtc)}_2(PHPh_2)_2]^+ \xrightarrow{k_3} cis\text{-[Co(dtc)}_2(PHPh_2)_2]^+$$
$$(5)$$

in which the rate constants, k_1, k_2, and k_3, correspond to the PHPh$_2$ dissociation step, to the structural change process from the square pyramidal (C_{4v}) intermediate to the trigonal bipyramidal (*TBPY*) transition state, and to the $[PHPh_2]_{free}$-

Table 2 *Trans* to *cis* isomerization rate constants (k_{obs}/s^{-1}) obtained under various experimental conditions[a]

| T/K[b] | [PHPh$_2$]$_{added}$/mmol kg^{-1} | | | | |
	18.9	28.1	38.9	47.6	79.4
313.3	$(2.55 \pm 0.03) \times 10^{-5}$	$(2.35 \pm 0.02) \times 10^{-5}$	$(2.48 \pm 0.03) \times 10^{-5}$	$(2.55 \pm 0.03) \times 10^{-5}$	$(2.32 \pm 0.06) \times 10^{-5}$
318.2	$(5.17 \pm 0.13) \times 10^{-5}$		$(4.76 \pm 0.09) \times 10^{-5}$		$(5.40 \pm 0.10) \times 10^{-5}$
323.3	$(1.08 \pm 0.04) \times 10^{-4}$	$(1.09 \pm 0.04) \times 10^{-4}$	$(1.04 \pm 0.04) \times 10^{-4}$	$(1.02 \pm 0.02) \times 10^{-4}$	$(1.00 \pm 0.02) \times 10^{-4}$
328.2	$(2.18 \pm 0.08) \times 10^{-4}$	$(1.94 \pm 0.04) \times 10^{-4}$	$(2.12 \pm 0.08) \times 10^{-4}$		$(1.97 \pm 0.07) \times 10^{-4}$
333.4	$(4.68 \pm 0.06) \times 10^{-4}$	$(4.29 \pm 0.06) \times 10^{-4}$	$(4.20 \pm 0.05) \times 10^{-4}$	$(4.01 \pm 0.06) \times 10^{-4}$	$(4.09 \pm 0.05) \times 10^{-4}$

[a] The concentration of [Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ was adjusted to 1 mmol kg^{-1} for all samples. Ionic strength of the solutions was adjusted to 0.1 mol kg^{-1} by using tetra-*n*-butylammonium tetrafluoroborate. [b] The temperature of all sample solutions was held constant within ± 0.2 K.
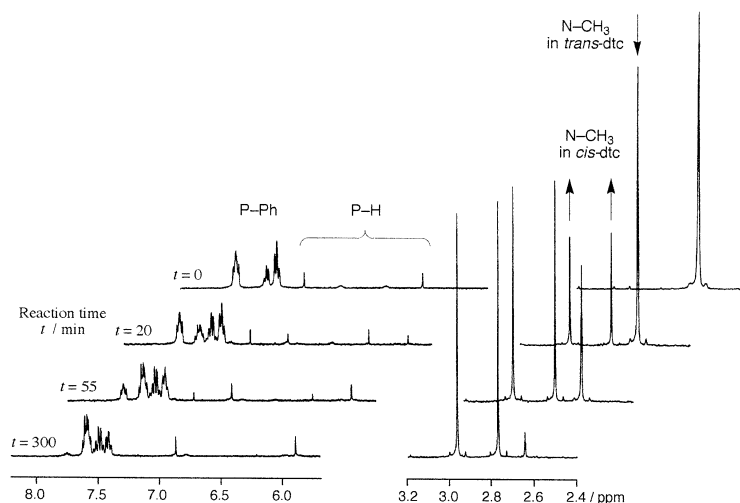
Fig. 4 ^{1}H NMR spectral change for the *trans* to *cis* thermal isomerization reaction of [Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ complexes at 333 K in acetonitrile-d_3. [Co(dtc)$_2$(PHPh$_2$)$_2$$^+$] = 0.01 mol kg^{-1}. CF$_3SO_3$Na (0.1 mol kg^{-1}) was used as the supporting electrolyte.

Fig. 5 Absorption spectral change for the *trans* to *cis* thermal isomerization reaction of [Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ complexes at 318 K in acetonitrile. [Co(dtc)$_2$(PHPh$_2$)$_2$$^+$] = 1.0 mmol kg^{-1}. Tetra-*n*-butyl-ammonium tetrafluoroborate (0.1 mol kg^{-1}) was used as the supporting electrolyte.
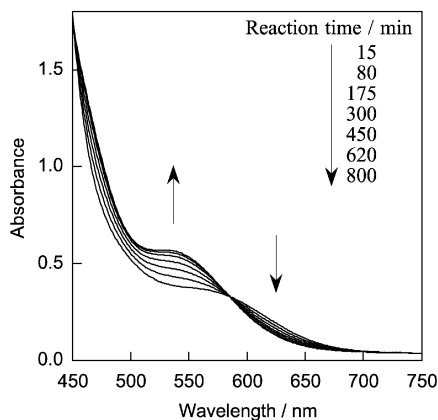
independent intramolecular twist process, respectively. By assuming a steady-state for the *trans*-[Co(dtc)$_2$(PHPh$_2$)]$^+$ (C_{4v}) species, the following rate law is derived.

$$-\frac{d[\textit{trans}\text{-Co(dtc)}_2(\text{PHPh}_2)_2]}{dt} = k_{obs}[\textit{trans}\text{-Co(dtc)}_2(\text{PHPh}_2)_2]$$

$$(6)$$

$$k_{obs} = \frac{k_1 k_2}{(k_{-1}[\text{PHPh}_2]_{free} + k_2)} + k_3$$

As k_2 corresponds to the deformation process from the square pyramidal intermediate to the trigonal bipyramidal transition state, the activation energy is expected to be very large for low-
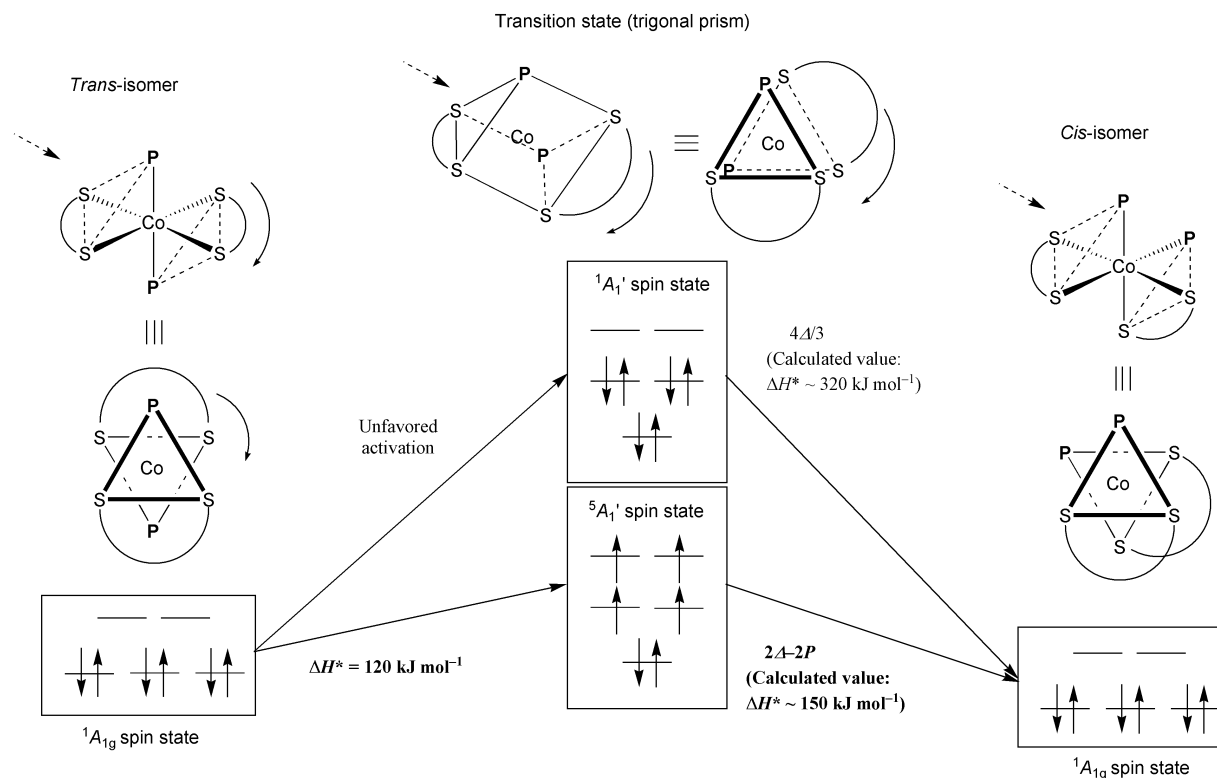
spin d^6 species in a strong field as reported by Vanquickenborne and Pierloot.[15] On the other hand, the k_{-1} should be large. Therefore, eqn. (6) is reduced to eqn. (7) under the experimental conditions.

$$k_{obs} = k_1 k_2/k_{-1}[\text{PHPh}_2]_{free} + k_3 \qquad (7)$$

It is obvious, from Table 2, that the apparent rate constant for the *trans* to *cis* isomerization reaction is independent of the concentration of added free PHPh$_2$, when [PHPh$_2$]$_{free}$ $\geqslant$ 15 mmol kg^{-1}. The lack of dependence of k_{obs} on [PHPh$_2$]$_{free}$ strongly indicates that the dissociation mechanism expressed by reactions (3) and (4) is not important when sufficient amounts of free PHPh$_2$ exist in the bulk. This result is consistent with the NMR observation: no appreciable dissociation of coordinated PHPh$_2$ from *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$.[23] As noted in the Appendices, the isomerization process initiated by the slow release of the P–H proton from coordinated PHPh$_2$ should also be completely suppressed by the addition of excess free PHPh$_2$ in the bulk. Therefore, it is concluded that the observed [PHPh$_2$]$_{free}$-independent rate constants for the *trans* to *cis* isomerization reaction correspond to an intramolecular process.

The ln k_{obs} *vs.* 1/T plot for the reactions with excess free PHPh$_2$ is linear over the examined temperature range, indicating that the isomerization takes place through a single reaction mechanism: the intramolecular twist mechanism corresponding to the k_3 process. The estimated activation parameters for this process are $\Delta H^* = 120 \pm 1$ kJ mol^{-1} and $\Delta S^* = 50 \pm 18$ J mol^{-1} K^{-1}.

The *trans* to *cis* isomerization without dissociation of coordinated PHPh$_2$ may proceed through a Ray–Dutt type twisting mechanism as shown in Scheme 1.[13,24,25] The relatively large activation enthalpy as well as the near-zero activation entropy for this reaction supports the intramolecular twist

Transition state (trigonal prism)

Trans-isomer

Cis-isomer

$^1A_1'$ spin state

$4\Delta/3$
(Calculated value:
$\Delta H^* \sim 320$ kJ mol^{-1})

Unfavored
activation

$^5A_1'$ spin state

$\Delta H^* = 120$ kJ mol^{-1}

$2\Delta - 2P$
(Calculated value:
$\Delta H^* \sim 150$ kJ mol^{-1})

$^1A_{1g}$ spin state

$^1A_{1g}$ spin state

Scheme 1 Energy diagram for the *trans* to *cis* isomerization reaction of [Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ through the twist mechanism. Δ: ligand-field parameter; P: spin-pairing energy.

mechanism similar to the processes observed for the isomerization reactions of [Ni(en)$_3$]$^{2+}$ and [Ni(o-phen)$_3$]$^{2+}$ complexes (en = ethylenediamine, o-phen = 1,10-phenanthroline).[13,26,27]

The activation enthalpy for such a twist mechanism may be estimated on the basis of the ligand field theory: the energy difference between the pseudo-octahedral structure in the ground state and the trigonal prism structure in the transition state depends on the spin multiplicity in the transition state. Vanquickenborne and Pierloot[14,15] derived activation free energies for the isomerization reactions by the intramolecular twist mechanism for d^6 low-spin cobalt(III) and iron(II) in a strong field, and concluded that the reactions require a change in the spin state. Although their discussion is based on the AOM calculation, a rough estimation of the activation energy is also possible by using the ligand-field parameter Δ and the mean spin-pairing energy P.

We consider the reaction from the direction of *cis* to *trans* isomerization because the Δ value for the *trans* complex is not available. The activation enthalpy corresponding to the formation of the trigonal prismatic transition state (in the $^1A_1'$ spin singlet state) from the $^1A_{1g}$ ground state may be roughly expressed by $4\Delta/3$, according to AOM. Then, the activation enthalpy is estimated as *ca.* 320 kJ mol^{-1} for the isomerization of *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ to *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$. On the other hand, if the transition state is in the spin quintet state ($^5A_1'$), the activation enthalpy may be roughly expressed as $2\Delta - 2P$. The activation enthalpy from *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ in the $^1A_{1g}$ ground state to the $^5A_1'$ trigonal prismatic transition state is then far smaller than that for the activation process with no spin state change, although the P value for a d^6 configuration is somewhat reduced to a value less than 20000 cm^{-1} depending on the decrease in the inter-electronic repulsion.[28] It is evident, therefore, that the twist process with change in the spin multiplicity is the more favored for the *cis* to *trans* isomerization of [Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$, although the rough nature of this kind of calculation may not provide a reliable activation enthalpy (Scheme 1).[29]

Such a change in the spin state can be rationalized by the fact that the time required to achieve low-spin/high-spin

equilibrium in a given geometry is very short (10^{-9} s).[30–33] Therefore, it is possible to conclude that the thermal *trans* to *cis* isomerization of [Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ takes place *via* the Ray–Dutt twist mechanism with a change in the spin multiplicity, by considering the principle of microscopic reversibility. The photo-induced *cis* to *trans* isomerization process may also proceed through the spin-quintet state with its pseudo-trigonal prismatic configuration after spin-allowed $^1A_{1g} \longrightarrow {}^1T_{1,2g}$ (d–d) excitation: the excited singlet state in the pseudo-octahedral configuration lies some 100 kJ mol^{-1} above the pseudo-trigonal prismatic transition state with a spin-multiplicity of five.

No appreciable dissociation of diphenylphosphine from the singly charged [Co(dtc)$_2$]$^+$ moiety indicates that the bonding between cobalt(III) and diphenylphosphine is very strong: low-spin cobalt(III) complexes with reduced net charge usually exhibit much larger aquation and ligand substitution rate constants.[34] Why then, is the *cis* complex thermodynamically the more preferred? The contribution of the stacking interaction between one of the phenyl rings on PHPh$_2$ and the Co–dtc plane as observed in the crystal structure of the *cis* complex may not be important, as the free energy of stabilization by such stacking interactions are usually much less than 10 kJ mol^{-1}.[35] A similar thermodynamic preference for *cis* coordination was reported for the d^6 Ru(II) and Os(II) complexes with triphenylphosphine.[36,37] Chakravorty and co-workers concluded that the *cis* preference in these complexes was attributed to the filled t$_{2g}$ orbitals: *i.e.* effective π-back donation to the triphenylphosphine ligand coupled with the strong donicity of dtc$^-$ ligands stabilizes the *cis*-isomer. If such an explanation is correct, then the ligand-field splittings, Δ, for the *cis*- and *trans*-isomers have to be significantly different; we expect *ca.* 30 kJ mol^{-1} (= 2500 cm^{-1}) for $\Delta G°$ corresponding to the equilibrium expressed by $K = [cis\text{-}Co(III)]/[trans\text{-}Co(III)] > 10^4$ at 333 K. It is likely that the ligand-field for *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ is some 2500 cm^{-1} smaller than that for *cis*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$, although it was not possible to estimate the exact Δ value for the *trans*-isomer as no clear second d–d band was observed for this species. The electrochemical observation confirmed that the LUMO levels of *cis*- and *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ are the
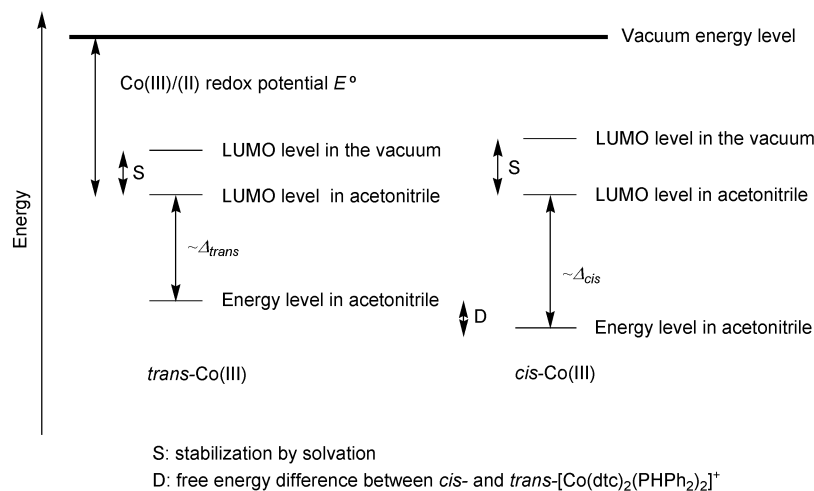
Scheme 2 Energy balance of the *cis*- and *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ complexes in acetonitrile.

same in acetonitrile within the experimental uncertainty. This may be explained by the difference in contribution of the solvation free energy; *cis*-cobalt(III) species with a larger dipole moment than *trans*-cobalt(III) experience more stabilization than *trans*-cobalt(III) in polar solvents such as acetonitrile, while the difference in the solvation energies is less significant for *cis*- and *trans*-cobalt(II) species because they carry no charge. Therefore, the LUMO energy level (antibonding σ* level) of *cis*-cobalt(III) is lowered to almost the same as that of *trans*-cobalt(III) in acetonitrile (Scheme 2).

Conclusion

In this article, we reported the synthesis and structural characterization of novel *cis*- and *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ and the kinetics of the thermal *trans* to *cis* isomerization reaction in acetonitrile. There was no apparently reasonable relationship between the structural parameters (Co–P lengths and P–Co–P angles) and σ-donicity for a series of phosphine ligands, unless a significant contribution from π-back bonding was taken into account. The thermodynamic and kinetic stability of the Co–P bond in the mutually *trans* positions of [Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$ may also be reasonably explained when π-acidity is admitted for the secondary phosphines. Therefore, we conclude that even PHPh$_2$ exhibits π-acidity and that the interplay of Tolman's cone angle, σ-donicity and π-acidity determines the stability of the complexes and bond lengths between cobalt(III) and phosphines.

We also found that the existence of trace amounts of water in the solvents induces dissociation of the P–H proton from coordinated PHPh$_2$, that causes multi-exponential kinetic behavior when no free PHPH$_2$ is added to suppress the activity of water. From the kinetic analyses of the thermal *trans* to *cis* isomerization reactions with excess free PHPh$_2$, we successfully extracted the kinetic parameters corresponding to the intramolecular twist process *via* the trigonal prismatic transition state with a spin multiplicity of five.

Appendix 1

The P–H proton signals of coordinated PHPh$_2$ in methanol-d_4 which contains *ca.* 10 mmol kg^{-1} of water gradually disappeared at a very slow rate ($< 1 \times 10^{-5}$ s^{-1}). Although isomerization was observed even in such "wet" methanol, it was not possible to describe the reaction by simple first-order kinetics. On the other hand, isomerization with *ca.* 10^{-5} s^{-1} was observed in dry methanol (water content was *ca.* 1 mmol kg^{-1}: the isomerization process was monitored *via* the dtc$^-$ signals in both cases). Moreover, a first-order isomerization process with an identical rate constant to that observed in dry methanol

was also observed in "wet" methanol with excess amounts (10–100 mmol kg^{-1}) of free PHPh$_2$. After completion of the isomerization reaction, we observed the P–H proton signals corresponding to PHPh$_2$ on the *cis* isomer in these sample solutions. Therefore, it is indicated that the trace amount of water in these solvents causes slow abstraction of the P–H proton on coordinated PHPh$_2$ and the added free PHPh$_2$ suppresses such a reaction. Results of the following additional experiment support the proton abstraction reaction from coordinated PHPh$_2$.

Addition of distilled triethylamine to the methanol and acetonitrile solutions containing *trans* complex immediately induced a color change ($\ll$ 1s). A strong base such as triethylamine may either abstract the P–H proton from coordinated PHPh$_2$ or substitute coordinated ligands. By considering the expected dissociative character of a d^6 low-spin Co(III) center, an associative attack by the added amine is not likely to occur. After abstraction of the P–H proton, isomerization of the phosphide-coordinated *trans* complex takes place, giving multi-exponential kinetic traces as observed for the sample solutions without added free PHPh$_2$ (see Appendix 2). The activation barrier for such a process may be somewhat larger than that for the isomerization of *trans*-[Co(dtc)$_2$(PHPh$_2$)$_2$]$^+$, by considering the larger ligand-field expected for the more basic phosphide ligand.

The rate constant for the isomerization reaction in methanol with excess PHPh$_2$ was identical to that for the reaction in acetonitrile with excess free PHPh$_2$. Such observations confirm that addition of free PHPh$_2$ do make the reaction trace first-order in these solvents (methanol and acetonitrile), and the observed isomerization rate constants with excess PHPh$_2$ are almost identical in acetonitrile and in methanol. These results, together with the fact that an identical isomerization rate constant was obtained in dry chloroform without addition of free PHPh$_2$, indicate that the observed processes in acetonitrile and in methanol with excess PHPh$_2$ proceed through the twist mechanism: a dissociation process is more prone to be influenced by the difference in the dielectric nature of solvents.

However, we may not be able to discard the possible participation of the dissociative isomerization pathway. If the dissociative isomerization mechanism is operative, which is initiated by the cleavage of either Co(III)–P or one Co(III)–S bond, the succeeding process involves the square-pyramidal to trigonal-bipyramidal structural change. According to the AOM calculation, we can safely predict that such a conformational change requires a much larger activation enthalpy and cannot compete with the twist process. However, it has been predicted by Vanquickenborne and Pierloot[13–15] that the π-basicity of the coordinated spectator ligands significantly reduces the barrier for such a structural change. Without addition of free PHPh$_2$,
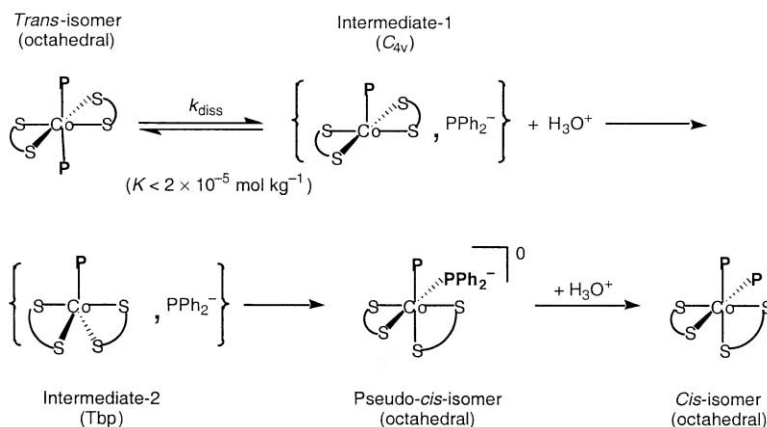
Scheme 3

the product of the isomerization reaction was mostly the *cis* isomer in acetonitrile with a small amount of water. As few other ^{1}H signals were observed, decomposition of the *cis* and *trans* complexes was minimal. We describe the possible mechanism that ensures retention of the $[Co(dtc)_2]^+$ frame even after dissociation of PHPh$_2$ in Appendix 2.

We therefore conclude that the multi-exponential process observed for the samples without free PHPh$_2$ is attributed to (a) participation of the isomerization process initiated by the hydrogen abstraction reaction by a trace amount of water, (b) dissociative isomerization initiated by the dissociation of coordinated PHPh$_2$ and/or (c) dissociative isomerization initiated by the bond cleavage of one of the Co(III)–S(dtc$^-$) bonds. Although mechanisms (b) and (c) may not be energetically favored, we do not have sufficient experimental evidence to discard the possibility of these processes. Addition of excess free PHPh$_2$ suppresses both (a) and (b) either by "chewing-up" the trace amount of water or by reducing the degree of dissociation of coordinated PHPh$_2$. When sufficient amounts of PHPh$_2$ were added to the reaction mixture, mechanisms (a) and (b) may not become significant, as described in the text. However, mechanism (c) is still a candidate for the current isomerization reaction. An experimental result that the rate constant was not influenced by the difference of solvents and supporting electrolytes supports the idea that such a mechanism may not be important for the current isomerization reaction; pathway (c) with a rate-limiting charge separation process may be largely influenced by the polarity of solvents as well as the ionic circumstances (*i.e.* ionic strengths, different salts, *etc.*) may not support this mechanism.

Appendix 2

The dissociation of coordinated PHPh$_2$ is expressed by the following equilibrium:

$$trans\text{-}[Co(dtc)_2(PHPh_2)_2]^+ \xrightarrow{K}$$
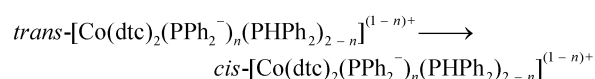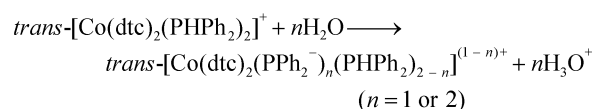$$[Co(dtc)_2(PHPh_2)]^+ + PHPh_2$$
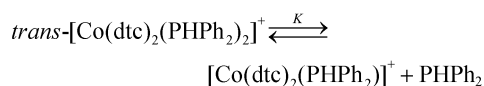
Though the equilibrium constant may be very small, the dissociation rate constant is not necessarily small. From the NMR evidence that no free PHPh$_2$ was detected in a 10 mmol kg^{-1} solution of *trans*-$[Co(dtc)_2(PHPh_2)_2]^+$ when no appreciable amount of water was present, the equilibrium constant is estimated to be less than 2×10^{-5} mol kg^{-1}, by assuming that dissociation of PHPh$_2$ by less than 5% cannot be detected by the NMR instrument.

The square pyramidal intermediate produced by the dissociation of coordinated PHPh$_2$ may undergo isomerization through the formation of a trigonal bipyramidal intermediate. However, such a reaction may not produce the expected *cis*-

isomer unless sufficient amounts of free PHPh$_2$ exist in the bulk. Without free PHPh$_2$ in the bulk, a further decomposition of the intermediate may be more likely to occur. If these processes compete with the isomerization *via* the twist mechanism, the absorption change has to be explained by first-order kinetics (parallel first-order processes in which one leads to the *cis* isomer and another leads to rapid decomposition), without exhibiting the isosbestic points. Therefore, we presume that the $[Co(dtc)_2]^+$ frame is retained even on dissociation of PHPh$_2$ because of the strong propensity of dtc$^-$ to produce tris-coordinated complexes with Co(III), and the final product of such a decomposition reaction must have a similar structure to that of *cis*-$[Co(dtc)_2(PHPh_2)_2]^+$ to exhibit clear isosbestic points.

With the existence of *ca.* 5 mmol kg^{-1} water in the bulk, a rapid dissociation of a P–H proton in free PHPh$_2$ takes place as noted in the section of the NMR measurements. Therefore, it is likely that dissociated PHPh$_2$ is deprotonated in the immediate vicinity of the parent cobalt complex, forming a {$[Co(dtc)_2(PHPh_2)]^+$, PPh$_2^-$} ion pair in a solvent with a small dielectric constant such as acetonitrile. This ion pair, then, undergoes structural change to form trigonal bipyramidal intermediate-2, followed by the rapid formation of *cis*-$[Co(dtc)_2(PHPh_2)(PPh_2^-)]^0$ as shown in Scheme 3. The absorption spectrum of *cis*-$[Co(dtc)_2(PHPh_2)(PPh_2^-)]^0$ may not be very different from that for *cis*-$[Co(dtc)_2(PHPh_2)_2]^+$, as the phenyl groups in PHPh$_2$ act as the electron sponge. In the end, it is likely that *cis*-$[Co(dtc)_2(PHPh_2)(PPh_2^-)]^0$ is protonated again to produce *cis*-$[Co(dtc)_2(PHPh_2)(PHPh_2)]^+$, as the result of NMR measurements indicates that coordinated PHPh$_2$ may not strongly interact with bulk water in acetonitrile. It is, then, obvious that such a multi-step reaction, coupled with the ordinary one-step twisting mechanism, leads to multi-exponential kinetic traces with isosbestic points, as observed in this study.

A similar reaction process through the ion-pair formation is also possible when the proton abstraction from coordinated PHPh$_2$ rather than the dissociation of coordinated PHPh$_2$ takes place as the initial step of the reaction. In such a case, the succeeding isomerization process is described by the regular twist mechanism within the phosphide-coordinated *trans* complex. This twist process may be much slower than the water-assisted dissociation of the P–H proton from coordinated PHPh$_2$, and the observed kinetic trace may also become multi-exponential.

$$trans\text{-}[Co(dtc)_2(PHPh_2)_2]^+ + nH_2O \longrightarrow$$
$$trans\text{-}[Co(dtc)_2(PPh_2^-)_n(PHPh_2)_{2-n}]^{(1-n)+} + nH_3O^+$$
$$(n = 1 \text{ or } 2)$$

$$trans\text{-}[Co(dtc)_2(PPh_2^-)_n(PHPh_2)_{2-n}]^{(1-n)+} \longrightarrow$$
$$cis\text{-}[Co(dtc)_2(PPh_2^-)_n(PHPh_2)_{2-n}]^{(1-n)+}$$

The computer analyses of the reaction traces for the samples with $[PHPh_2]_{free} < 10$ mmol kg^{-1} certainly fit well to a double-exponential function. However, it is clear that any alternative multi-step mechanism similar to those described above also explains the observed multi-exponential behavior with isosbestic points. Therefore, we only report here, as a result of the double-exponential analyses, a tentative value of $k_{sum} = 10^{-4}$–10^{-5} s^{-1} at 333 K, which corresponds to the sum of the rate constants for all possible rate-determining steps: the PHPh$_2$ dissociation step for the dissociative isomerization, the hydrogen ion-abstraction step, and the unimolecular Ray–Dutt twisting step.

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