A Geometrical Isomeric Pair of Novel Cobalt(III) Complexes Containing Diphenylphosphine: *cis*- and *trans*-$[Co(dtc)_2(PHPh_2)_2]BF_4$ (dtc = *N*,*N*-Dimethyldithiocarbamate)

Takayoshi Suzuki,* Satoshi Iwatsuki,[†] Hideo D. Takagi,[†] and Kazuo Kashiwabara*[†]
Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka 560-0043
[†]*Department of Chemistry, Graduate School of Science, Nagoya University, Chikusa-ku, Nagoya 464-8602*

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The stable title cobalt(III) complexes containing $PHPh_2$ have been prepared and investigated for their crystal structures and spectroscopic properties. The *cis*-isomer was converted photochemically to the *trans*-isomer, which isomerized thermally to the original *cis*-isomer. The structural parameters and the ligand-field strengths of the $PHPh_2$ complexes were not predictable from the σ-donicity of $PHPh_2$.

Diphenylphosphine has been suggested to be a very weak σ-donor ligand with no π-bonding character, since the pK_a of its conjugate acid ($H_2PPh_2^+$) is very low (0.03) and the Giering's parameter χ_d = 17.35.[1] The pK_a value is much smaller than those of PMe_3 (pK_a = 8.65, χ_d = 8.55) and even $P(OMe)_3$ (pK_a = 2.60, χ_d = 16.70), indicating that Co(III)-$PHPh_2$ complexes may be thermodynamically more unstable than Co(III)-phosphite complexes. In fact, there have been only few Co(III) complexes coordinated with secondary phosphines: *trans*-$[CoHX(PHPh_2)_4]ClO_4$ (X = Cl or CN) and $[CoH(PHEt_2 \text{ or } PHEtPh)_5](BF_4)_2$,[2] which are unstable. Another intriguing feature of secondary phosphine complexes is kinetic instability to yield R_2P^--bridged di- or polynuclear species,[3,4] or an agostic M···H–P interaction.[4] Therefore, relatively few mononuclear transition-metal complexes containing $PHPh_2$ have been known,[5] in contrast to a large number of tertiary phosphine complexes. In this study we have examined the preparation and structural and chemical properties of Co(III)-$PHPh_2$ complexes with *N*,*N*-dimethyldithiocarbamate (dtc) auxiliary ligands, $[Co(dtc)_2(PHPh_2)_2]^+$ ($[\mathbf{1}]^+$), as an extension of our previous studies on Co(III)-phosphite[6] and/or Co(III)-tertiary phosphine[7] complexes in which dtc is suggested to be the best ligand to stabilize Co(III)–P bond due probably to its steric compactness and electronic softness.

A reaction of an orange ethanolic suspension (30 cm^3) containing $Co(BF_4)_2 \cdot 6H_2O$ (2.0 mmol) and $PHPh_2$ (4.9 mmol) with a solution of tetramethylthiuram disulfide (2.0 mmol) in ethanol /dichloromethane (3:1, 80 cm^3) in the dark gave a red precipitate with the composition, $Co(dtc)_2(PHPh_2)_2BF_4$, in 63% yield.[8] The observed ^{1}H NMR spectrum of the product in CD_2Cl_2 was consistent with the structure of *cis*-$[\mathbf{1}]^+$: 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, as shown in Figure 1(a). Recrystallization of the compound from acetonitrile/diethyl ether in the dark gave red purple crystals suitable for the single-crystal X-ray structure analysis,[9] which confirmed the molecular structure of the *cis*-isomer as shown in Figure 2(a).

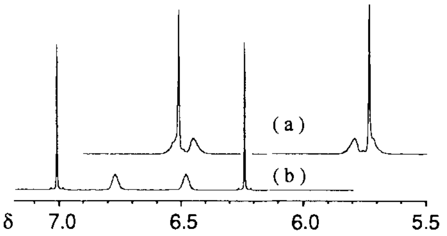

Figure 1. ^{1}H NMR (400 MHz) spectra in the region of P–H resonance of (a) *cis*- and (b) *trans*-$[\mathbf{1}]BF_4$ in CD_2Cl_2 at 30 °C (ref TMS).

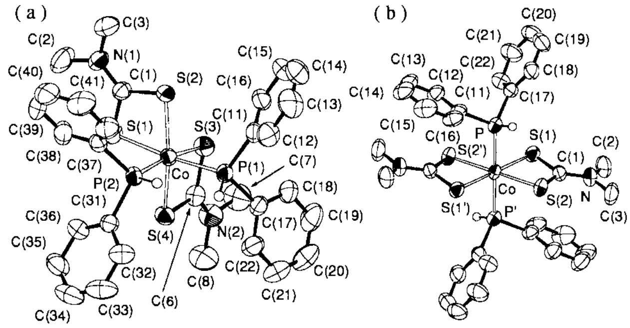

Figure 2. Perspective drawings (50% probability level) of the cationic parts of (a) *cis*-$[\mathbf{1}]BF_4 \cdot CH_3CN \cdot 0.5Et_2O$ and (b) *trans*-$[\mathbf{1}]BF_4$. Hydrogen atoms, except for those directly bound to P atoms, are omitted for clarity. Selected distances and angles: (a) Co–P(1) 2.2340(6), Co–P(2) 2.2258(7), Co–S(1) 2.2699(7), Co–S(2) 2.2684(6), Co–S(3) 2.2963(7), Co–S(4) 2.2577(6) Å; P(1)–Co–P(2) 90.51(2), S(1)–Co–S(2) 76.57(2), S(3)–Co–S(4) 76.47(2)°; (b) Co–P 2.276(1), Co–S(1) 2.269(1), C–S(2) 2.269(1) Å; S(1)–Co–S(2) 77.03(4)°.

When the solution of *cis*-$[\mathbf{1}]BF_4$ in dichloromethane was allowed to stand under a fluorescent 15-W desk lamp for several days, the complex isomerized almost quantitatively to the corresponding *trans*-isomer. The crystals of *trans*-$[\mathbf{1}]BF_4$[8] were deposited from a solution of *cis*-$[\mathbf{1}]BF_4$ in a 1:1 mixture of dichloromethane and toluene added a few drops of acetonitrile by evaporation in the open air on exposure to room light (15-W fluorescent desk lamp). The ^{1}H NMR spectrum of *trans*-$[\mathbf{1}]BF_4$ in CD_2Cl_2 showed 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, as shown in Figure 1(b). It should be noted that the $^1J_{P-H}$ coupling constant of the *trans*-isomer is smaller, but the $^3J_{P-H}$ is remarkably much larger, than those of the *cis*-isomer. The molecular structure of *trans*-$[\mathbf{1}]BF_4$ was also confirmed by X-ray analysis,[9] as shown in Figure 2(b). It was also found that the *trans*-isomer was reconverted thermally to the original *cis*-isomer, when the solution was heated to 40 °C in the dark for 1 day. The isomerization was accompanied by a slight decomposition of the complex, yielding uncharacterized species and free $PHPh_2$. However, by addition of excess free $PHPh_2$ to the solution the *cis*-isomer was reconverted almost quantitatively. The kinetic studies of the thermal isomerization are currently in progress.

In the structure of *cis*-[**1**]BF_4 (Figure 2(a)), two phenyl rings of $PHPh_2$ are oriented in the way that the intramolecular steric interaction between two adjacent $PHPh_2$ ligands is minimized. The stacking interactions between the dtc plane and one of the phenyl rings of $PHPh_2$ were also indicated. The average Co–P bond length in *cis*-[**1**]BF_4 is 2.230 Å, which is shorter than that (2.272 Å) in *cis*-$[Co(dtc)_2(PMe_2Ph)_2]PF_6$[7] having PMe_2Ph with a smaller steric requirement (Tolman's cone angle, $\theta = 122°$)[10] and a stronger σ-donicity ($\chi_d = 10.60$) than $PHPh_2$ ($\theta = 126°$, $\chi_d = 17.35$). The corresponding Co–P bond lengths in the analogous PMe_3 ($\theta = 118°$, $\chi_d = 8.55$) and $P(OMe)Ph_2$ ($\theta = 132°$, $\chi_d = 14.82$) complexes are 2.200 and 2.245 Å, respectively.[7] Furthermore, the P(1)–Co–P(2) angle in *cis*-[**1**]BF_4, 90.51(2)°, is significantly smaller than those in the above *cis*-$[Co(dtc)_2(P\text{-ligand})_2]^+$-type complexes: 96.8(1)° for PMe_3, 95.14(2)° for PMe_2Ph, and 92.68(4)° for $P(OMe)Ph_2$. It appears that there is no reasonably simple relationship between these structural parameters (Co–P bond length and P–Co–P angle) and either the Tolman's cone angle or the σ-donicity of P-ligands. Probably, on the basis of the observed conformation of three substituents of $PHPh_2$, the negligibly small steric requirement of the H substituent reduces steric congestion around the Co center more effectively than that expected from the Tolman's cone angle.

For *trans*-$[Co(dtc)_2(P\text{-ligand})_2]^+$, the above-mentioned complexity arised from steric congestion would be ignored because of the mutual *trans* configuration of two P-ligands. The electronic *trans* influence, in addition to the steric requirement (termed by the cone angle), of P-ligand must be taken into consideration for comparison of the Co–P bond lengths.[11] In fact, the comparable Co–P bond lengths in *trans*-$[Co(dtc)_2(PMe_3)_2]BF_4$ (2.287(1) Å) and *trans*-$[Co(dtc)_2(PMe_2Ph)_2]BF_4$ (2.2843(8) Å) are resulted from competition of the mutual electronic *trans* influence with the steric requirement.[7] Despite a larger cone angle of $PHPh_2$ than those of PMe_3 and PMe_2Ph, the Co–P bond length in *trans*-[**1**]BF_4, 2.276(1) Å, is also comparable to (or even slightly shorter than) those in the above PMe_3 and PMe_2Ph complexes, which is also indicative of a significant contribution of electronic *trans* influence to the Co–P bond lengths. The influence of $PHPh_2$ would be not as small as expected from the very weak σ-donicity of $PHPh_2$, since the Co–P bond in *trans*-[**1**]BF_4 is appreciably longer (by 0.046 Å) than that in *cis*-[**1**]BF_4.

The UV–vis absorption spectrum of *cis*-[**1**]BF_4 in CH_2Cl_2 is similar to that of *cis*-$[Co(dtc)_2(PMe_3 \text{ or } PMe_2Ph)_2](BF_4 \text{ or } PF_6)$ (Figure 3(a)).[7] The $PHPh_2$ complex, *cis*-[**1**]$^+$, shows two bands at 18430 and 23430 cm^{-1}, which are assignable as the first and the second d–d transition bands, respectively.[6,7] The ligand-field strength, Δ, and the Racah's interelectronic repulsion parameter, B, of *cis*-[**1**]$^+$ are estimated[12] as 19680 and 313 cm^{-1}, and those of the PMe_3 and PMe_2Ph complexes as 19580 and 311; 19170 and 316 cm^{-1}, respectively, indicating that the ligand-field strength of $PHPh_2$ is a little stronger than those of PMe_3 and PMe_2Ph, in contrast to the much weaker σ-donicity of $PHPh_2$.

The absorption spectrum of *trans*-[**1**]BF_4 (Figure 3(b)) gives the a^1E_g component of the first d–d transition band at 17300 cm^{-1} and the lowest energy LMCT transition band at 24920 cm^{-1}. The corresponding bands of *trans*-$[Co(dtc)_2(P\text{-ligand})_2]BF_4$ were observed at 17900 and 27380; 17170 and 25570; 16580 and 24770; and 15740 and 23080 cm^{-1} for the PMe_3, PMe_2Ph, $PMePh_2$, and PPh_3 complexes, respectively.[7] It seems that the ligand-field perturbation energy of $PHPh_2$ is not as small as the one expected from the σ-donicity, but correlates to the steric bulkiness (Tolman's cone angle) of the phosphines: $PMe_3 < PMe_2Ph \leq PHPh_2 < PMePh_2 < PPh_3$.

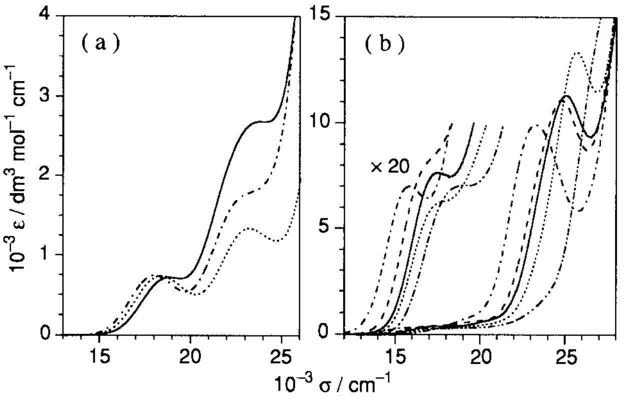

Figure 3. UV–vis absorption spectra of (a) *cis*-$[Co(dtc)_2(PHPh_2)_2]BF_4$ (————), *cis*-$[Co(dtc)_2(PMe_3)_2]BF_4$ (- - - - - - -), and *cis*-$[Co(dtc)_2(PMe_2Ph)_2]PF_6$ (— • — • —); (b) *trans*-$[Co(dtc)_2(P\text{-ligand})_2]BF_4$ {P-ligand = $PHPh_2$ (————), PMe_3 (— • • — • •), PMe_2Ph (- - - - - - -), $PMePh_2$ (— — —), and PPh_3 (— • — • —)} in CH_2Cl_2 at room temperature.

In summary, the Co(III)-$PHPh_2$ complexes of *cis*- and *trans*-[**1**]BF_4 exhibit unexpectedly high stabilities, short Co–P bond lengths, and strong ligand-field strengths from a very weak σ-donicity of $PHPh_2$.

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8 Found for *cis*-[**1**]BF_4: C, 47.20; H, 4.49; N, 4.03%. Found for *trans*-[**1**]BF_4: C, 47.09; H, 4.41; N, 3.79%. Calcd for $C_{30}H_{34}BCoF_4N_2P_2S_4$: C, 47.50; H, 4.52; N, 3.69%.
9 *cis*-[**1**]$BF_4 \cdot CH_3CN \cdot 0.5Et_2O$; fw = 836.63, Rigaku Raxis-rapid (23 °C, $\lambda(\text{Mo K}_\alpha) = 0.71073$ Å), monoclinic, $P2/n$ (no. 13), $a = 19.359(1)$, $b = 11.1101(7)$, $c = 20.642(1)$ Å, $\beta = 115.830(2)°$, $U = 2996.3(4)$ Å^3, $Z = 4$, $D_x = 1.391$ Mg m^{-3}, 9084 independent reflns ($2\theta \leq 55°$), $R_1(F^2: F^2 > 2\sigma(F^2)) = 0.040$, $wR2(F^2$: all reflns$) = 0.117$. *trans*-[**1**]BF_4; fw = 758.51, Rigaku AFC-5R (23 °C, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å), monoclinic, $C2/c$ (no. 15), $a = 19.507(4)$, $b = 14.529(5)$, $c = 14.445(3)$ Å, $\beta = 122.20(1)°$, $U = 3464(1)$ Å^3, $Z = 4$, $D_x = 1.454$ Mg m^{-3}, 5070 independent reflns ($2\theta \leq 60°$), $R_1(F^2: F^2 > 2\sigma(F^2)) = 0.055$, $wR_2(F^2$: all reflns$) = 0.147$.
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