

A Geometrical Isomeric Pair of Novel Cobalt(III) Complexes Containing Diphenylphosphine: *cis*- and *trans*-[Co(dtc)₂(PPh₂)₂]BF₄ (dtc = *N,N*-Dimethyldithiocarbamate)

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The stable title cobalt(III) complexes containing PPh₂ 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 PPh₂ complexes were not predictable from the σ -donicity of PPh₂.

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 (H₂PPh₂⁺) is very low (0.03) and the Giering's parameter $\chi_d = 17.35$.¹ The pK_a value is much smaller than those of PMe₃ ($pK_a = 8.65$, $\chi_d = 8.55$) and even P(OMe)₃ ($pK_a = 2.60$, $\chi_d = 16.70$), indicating that Co(III)-PPh₂ 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(PPh₂)₄]ClO₄ (X = Cl or CN) and [CoH(PHEt₂ or PHEtPh)₅](BF₄)₂,² which are unstable. Another intriguing feature of secondary phosphine complexes is kinetic instability to yield R₂P-bridged di- or polynuclear species,^{3,4} or an agostic M...H-P interaction.⁴ Therefore, relatively few mononuclear transition-metal complexes containing PPh₂ 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)-PPh₂ complexes with *N,N*-dimethyldithiocarbamate (dtc) auxiliary ligands, [Co(dtc)₂(PPh₂)₂]⁺ ([1]⁺), as an extension of our previous studies on Co(III)-phosphite⁶ and/or Co(III)-tertiary phosphine⁷ 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 cm³) containing Co(BF₄)₂·6H₂O (2.0 mmol) and PPh₂ (4.9 mmol) with a solution of tetramethylthiuram disulfide (2.0 mmol) in ethanol/dichloromethane (3:1, 80 cm³) in the dark gave a red precipitate with the composition, Co(dtc)₂(PPh₂)₂BF₄, in 63% yield.⁸ The observed ¹H NMR spectrum of the product in CD₂Cl₂ was consistent with the structure of *cis*-[1]⁺: two singlet resonances at δ 2.781 and 2.936 for N-CH₃. 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).

When the solution of *cis*-[1]BF₄ in dichloromethane was allowed to stand under a fluorescent 15-W desk lamp for several days, the complex isomerized almost quantitatively to the

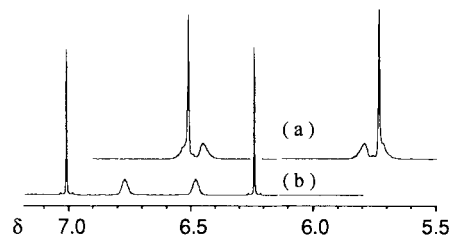


Figure 1. ¹H NMR (400 MHz) spectra in the region of P-H resonance of (a) *cis*- and (b) *trans*-[1]BF₄ in CD₂Cl₂ at 30 °C (ref TMS).

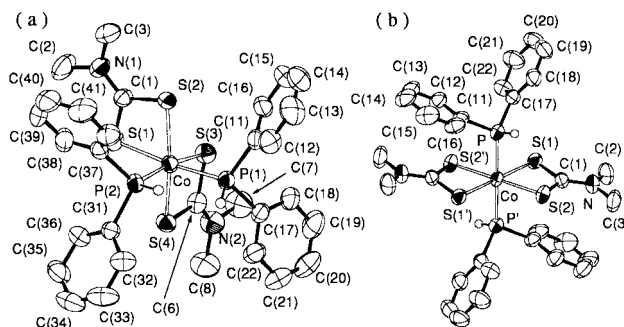


Figure 2. Perspective drawings (50% probability level) of the cationic parts of (a) *cis*-[1]BF₄·CH₃CN·0.5Et₂O and (b) *trans*-[1]BF₄. Hydrogen atoms, except for those directly bound to P atoms, are omitted for clarity. Selected distances and angles: (a) Co-P(1) 2.2340(6), Co-P(2) 2.2258(7), Co-S(1) 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), Co-S(2) 2.269(1) Å; S(1)-Co-S(2) 77.03(4)°.

corresponding *trans*-isomer. The crystals of *trans*-[1]BF₄⁸ were deposited from a solution of *cis*-[1]BF₄ 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 ¹H NMR spectrum of *trans*-[1]BF₄ in CD₂Cl₂ showed a singlet resonance at δ 2.585 for N-CH₃, 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*-[1]BF₄ 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 PPh₂. However, by addition of excess free PPh₂ 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]BF₄ (Figure 2(a)), two phenyl rings of PPhPh₂ are oriented in the way that the intramolecular steric interaction between two adjacent PPhPh₂ ligands is minimized. The stacking interactions between the dtc plane and one of the phenyl rings of PPhPh₂ were also indicated. The average Co–P bond length in *cis*-[1]BF₄ is 2.230 Å, which is shorter than that (2.272 Å) in *cis*-[Co(dtc)₂(PMe₂Ph)₂]PF₆⁷ having PMe₂Ph with a smaller steric requirement (Tolman's cone angle, $\theta = 122^\circ$)¹⁰ and a stronger σ -donicity ($\chi_d = 10.60$) than PPhPh₂ ($\theta = 126^\circ$, $\chi_d = 17.35$). The corresponding Co–P bond lengths in the analogous PMe₃ ($\theta = 118^\circ$, $\chi_d = 8.55$) and P(OMe)Ph₂ ($\theta = 132^\circ$, $\chi_d = 14.82$) complexes are 2.200 and 2.245 Å, respectively.⁷ Furthermore, the P(1)–Co–P(2) angle in *cis*-[1]BF₄, 90.51(2)°, is significantly smaller than those in the above *cis*-[Co(dtc)₂(P-ligand)₂]⁺-type complexes: 96.8(1)° for PMe₃, 95.14(2)° for PMe₂Ph, and 92.68(4)° for P(OMe)Ph₂. 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 PPhPh₂, 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-ligand)₂]⁺, the above-mentioned complexity arising 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(PMe₃)₂]BF₄ (2.287(1) Å) and *trans*-[Co(dtc)₂(PMe₂Ph)₂]BF₄ (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 PPhPh₂ than those of PMe₃ and PMe₂Ph, the Co–P bond length in *trans*-[1]BF₄, 2.276(1) Å, is also comparable to (or even slightly shorter than) those in the above PMe₃ and PMe₂Ph complexes, which is also indicative of a significant contribution of electronic *trans* influence to the Co–P bond lengths. The influence of PPhPh₂ would be not as small as expected from the very weak σ -donicity of PPhPh₂, since the Co–P bond in *trans*-[1]BF₄ is appreciably longer (by 0.046 Å) than that in *cis*-[1]BF₄.

The UV–vis absorption spectrum of *cis*-[1]BF₄ in CH₂Cl₂ is similar to that of *cis*-[Co(dtc)₂(PMe₃ or PMe₂Ph)₂](BF₄ or PF₆) (Figure 3(a)).⁷ The PPhPh₂ 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 estimated¹² as 19680 and 313 cm^{−1}, and those of the PMe₃ and PMe₂Ph complexes as 19580 and 311; 19170 and 316 cm^{−1}, respectively, indicating that the ligand-field strength of PPhPh₂ is a little stronger than those of PMe₃ and PMe₂Ph, in contrast to the much weaker σ -donicity of PPhPh₂.

The absorption spectrum of *trans*-[1]BF₄ (Figure 3(b)) gives the 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-ligand)₂]BF₄ were observed at 17900 and 27380; 17170 and 25570; 16580 and 24770; and 15740 and 23080 cm^{−1} for the

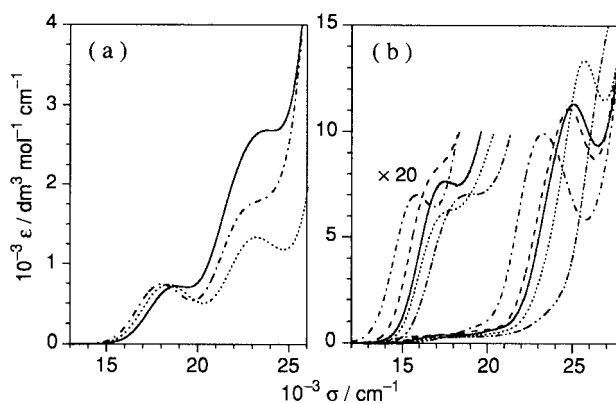


Figure 3. UV–vis absorption spectra of (a) *cis*-[Co(dtc)₂(PPhPh₂)₂]BF₄ (—), *cis*-[Co(dtc)₂(PMe₃)₂]BF₄ (---), and *cis*-[Co(dtc)₂(PMe₂Ph)₂]PF₆ (— · — · —); (b) *trans*-[Co(dtc)₂(P-ligand)₂]BF₄ {P-ligand = PPhPh₂ (—), PMe₃ (---), PMe₂Ph (— · — · —), PPhPh₂ (— — —)} in CH₂Cl₂ at room temperature.

PMe₃, PMe₂Ph, PMePh₂, and PPh₃ complexes, respectively.⁷ It seems that the ligand-field perturbation energy of PPhPh₂ 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: PMe₃ < PMe₂Ph ≤ PPhPh₂ < PMePh₂ < PPh₃.

In summary, the Co(III)-PPhPh₂ complexes of *cis*- and *trans*-[1]BF₄ exhibit unexpectedly high stabilities, short Co–P bond lengths, and strong ligand-field strengths from a very weak σ -donicity of PPhPh₂.

References and Notes

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- Found for *cis*-[1]BF₄: C, 47.20; H, 4.49; N, 4.03%. Found for *trans*-[1]BF₄: C, 47.09; H, 4.41; N, 3.79%. Calcd for C₃₀H₃₄BCoF₄N₂P₂S₄: C, 47.50; H, 4.52; N, 3.69%.
- cis*-[1]BF₄·CH₃CN·0.5Et₂O; fw = 836.63, Rigaku Raxis-rapid (23 °C, λ (Mo K α) = 0.71073 Å), monoclinic, P2₁/n (no. 13), $a = 19.359(1)$, $b = 11.1101(7)$, $c = 20.642(1)$ Å, $\beta = 115.830(2)^\circ$, $U = 2996.3(4)$ Å³, $Z = 4$, $D_x = 1.391$ Mg m^{−3}, 9084 independent reflns ($2\theta \leq 55^\circ$), $R_1(F^2)$: $F^2 > 2\sigma(F^2)$ = 0.040, $wR2(F^2)$: all reflns = 0.117. *trans*-[1]BF₄; fw = 758.51, Rigaku AFC-5R (23 °C, λ (Mo K α) = 0.71073 Å), monoclinic, C2/c (no. 15), $a = 19.507(4)$, $b = 14.529(5)$, $c = 14.445(3)$ Å, $\beta = 122.20(1)^\circ$, $U = 3464(1)$ Å³, $Z = 4$, $D_x = 1.454$ Mg m^{−3}, 5070 independent reflns ($2\theta \leq 60^\circ$), $R_1(F^2)$: $F^2 > 2\sigma(F^2)$ = 0.055, $wR2(F^2)$: all reflns = 0.147.
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- $C = 4B$ is assumed.