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Steric Effects Inhibiting Reactivity. Crystal and Molecular Structure, Spectra, and Chemistry of *trans*-Chlorocarbonylbis(tri-*o*-tolylphosphine)iridium(I) and Related Complexes[1]

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The title compound, *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$], is unreactive toward dihydrogen, dioxygen, sulfur dioxide, and cyanoolefins, and it undergoes only relatively slow oxidative addition reactions with hydrogen halides. This substantial inertness is in sharp contrast with the behavior of analogous tertiary phosphine (L) complexes, *trans*-[IrCl(CO)L$_2$], including those with L = (*p*- or *m*-tol)$_3$P, which readily form stable addition compounds with these small molecules. The infrared and electronic spectra of the title compound are, however, similar to those of the related *trans*-[IrCl(CO)L$_2$]. The lack of reactivity of *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] can be explained by the steric effects of the (*o*-tol)$_3$P ligands as revealed by the crystal and molecular structure determination. Two ortho CH$_3$ groups, one from each phosphine, are located near the apical positions (Ir–C = 3.55 Å) of the planar *trans*-IrCl(CO)P$_2$ unit. The crystals of the complex are monoclinic, with space group $P2_1/n$, a = 15.689 (6) Å, b = 10.981 (3) Å, c = 10.739 (4) Å, β = 92.93 (3)°, V = 1848 (2) Å^3, and Z = 2. Since the molecule was required to have a center of symmetry, the chlorine and carbonyl ligands were treated as randomly disordered. The structure was refined by full-matrix least squares to a final agreement residual of 0.047, based on 1230 observed reflections.

Introduction

The reversible coordination of small molecules to metal complexes continues to attract widespread attention. The factors which influence these reactions have been subject to much discussion which has mainly been concerned with the electronic properties of the reactants.[2] Recently, however, the importance of purely geometric aspects of the metal environment has become increasingly more recognized as evidenced, for instance, by an avalanche of notes reporting the reactions of several sterically obstructed iron complexes with molecular oxygen and related species.[3]

Our inquiries into the stereochemical properties of metal complexes affecting their addition reactions originate from the observations that some electronically similar iridium compounds show considerably different reactivities toward O$_2$, H$_2$, and related molecules (eq 1).[4,5] A striking example is the

$$trans\text{-}[\mathrm{IrCl(CO)L_2}] + \mathrm{XY} \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{(XY)IrCl(CO)L_2}] \qquad (1)$$

L = tertiary phosphine; XY = O_2, H_2, HCl, SO_2

title compound, *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] ((*o*-tol)$_3$P = tri-*o*-tolylphosphine, (*o*-CH$_3$C$_6$H$_4$)$_3$P), which has been found to be completely inert in solutions saturated with molecular oxygen or hydrogen at room temperature, although the physical properties of the complex closely resemble those of analogous iridium species (*trans*-[IrCl(CO)L$_2$]) displaying the well-established chemistry of low-valent and coordinatively unsaturated metal complexes (eq 1).[2] These observations led to the suggestion, based on molecular models, that the ortho CH$_3$ groups in *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] may effectively isolate the central atom from the attacking molecules.[4,5] In this paper we report the details of the crystal and molecular structure of the (*o*-tol)$_3$P complex, a quantitative comparison of its spectral and chemical properties with those of related compounds, and an analysis of steric effects inhibiting the reactivity of type d^8 complexes.

Experimental Section

Unless noted otherwise, reagent grade chemicals were used in all experiments.

Synthesis. *trans*-Chlorocarbonylbis(tri-*o*-tolylphosphine)iridium(I) has been prepared by two generally employed methods for the syntheses of *trans*-[IrCl(CO)L$_2$] derivatives.

(1)[6] IrCl$_3$(H$_2$O)$_n$ (0.345 g) and (*o*-tol)$_3$P (1.206 g, L:Ir = 4) were treated with water (25 ml) and diethylene glycol monomethyl ether (=DEGME, 100 ml), and the mixture was heated to boiling (108°) in an open beaker. As the water evaporated, the temperature rose to 193°, and the beaker was covered with a watch glass. The boiling–refluxing of the clear yellow solution was continued for ca. 3 hr while the volume of ca. 100 ml was maintained by occasional addition of DEGME. The watch glass was then removed; the solution was concentrated by evaporation to 45 ml and rapidly cooled to 0°. The resulting yellow precipitate was separated by filtration, washed with methanol and hexane, and dried in vacuo; the yield was 0.467 g or 55% based on Ir.

When somewhat modified conditions and shorter reaction times are applied, a different product is obtained which appears to be analogous to a previously reported unusual rhodium complex, "RhCl((*o*-tol)$_3$P)$_2$", formulated as RhCl[((*o*-tol)$_2$)PC$_6$H$_4$CH=CHC$_6$H$_4$P((*o*-tol)$_2$)].[7] Thus, a mixture of IrCl$_3$(H$_2$O)$_n$ (1.827 g) and (*o*-tol)$_3$P (7.8 g, L:Ir = 5) in DEGME (75 ml) was degassed and then refluxed under N$_2$ for 1 hr during which time the color of the red-brown suspension changed to orange. Filtration of the cooled mixture gave a yellow-orange solid and a yellow filtrate. The crystalline product was washed with ethanol and hexane and dried as before; 2.185 g was collected which corresponds to a 50% yield assuming "IrCl((*o*-tol)$_3$P)$_2$". The yellow filtrate was concentrated to 50 ml by heating in air, and 150 ml of methanol was added to produce a precipitate of *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] in 1.173 g or 26% yield.

(2) *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] was also synthesized by the procedure reported by Chatt et al.[8a] A solution of IrCl$_3$(H$_2$O)$_n$ (0.827 g) in 2-methoxyethanol (30 ml), saturated with carbon monoxide (1 atm), was refluxed at 124° for ca. 2 hr and cooled to 25°, and (*o*-tol)$_3$P (1.535 g, L:Ir = 2) was added. This reaction mixture (under CO atmosphere) was heated to boiling (ca. 124°, 10 min) and rapidly cooled to 15°; the resulting light yellow precipitate was separated by filtration, washed with methanol and hexane, and dried in vacuo; yield 1.778 g or 88%. The products of these experiments were often contaminated with [(H)(Cl)IrCl(CO)((*o*-tol)$_3$P)$_2$] (see Table VII), but a modified method[8b] gave pure samples. Thus, IrCl$_3$(H$_2$O)$_n$ (0.510 g) was dissolved in aqueous (10 ml) 2-methoxyethanol (45 ml) and the solution was refluxed for 4 hr while CO was passed through it. The solvent was then removed by evacuation, the residue dissolved in triethylamine (3 ml)–methanol (20 ml), (*o*-tol)$_3$P (1.915 g, L:Ir = 4) added, and the solution refluxed under N$_2$ for 3 hr. The resulting yellow powder was collected and treated as above; the yield was 0.812 g or 65%. Anal. Calcd for C$_{43}$H$_{42}$P$_2$OClIr: C, 59.77; H, 4.90; P, 7.17. Found: C, 59.42; H, 5.72; P, 7.50. The solid complex has been found unchanged after a 5-yr storage in air; for spectral properties, see Table V.

Crystals for X-ray study were obtained by dissolving a sample in

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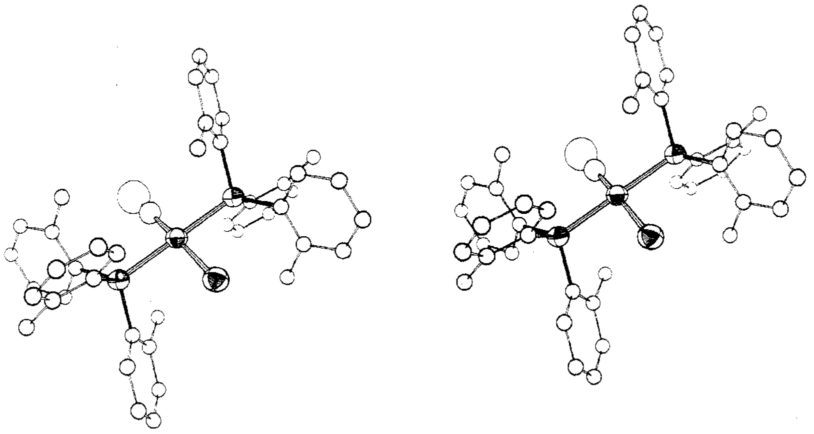

Figure 1. Stereoview of *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$]. The Cl and CO ligands are shown as being ordered for clarity.

a chloroform–benzene solution and allowing the solvent to evaporate in air at 25°.

Crystallographic Data and Solution and Refinement of the Structure. The structure was determined and refined by using routine methods. The crystal data, together with details of the data collection and structure determination and refinement, are summarized in Table I. The symmetry-required placement of the Ir atom at the origin resulted in an uneven distribution of diffracted intensity between the $h + k + l$ even and odd-parity groups. The former class contains 972 (79%) of the observed reflections, while the latter includes all but 6 of the unobserved reflections.

Spectral and Dynamic Measurements. The electronic absorption spectral data (Table V) were obtained on a Zeiss PMQ-II or Cary 14 spectrophotometer as follows. (a) Ca. 10^{-4} *M* solutions of *trans*-[IrCl(CO)L$_2$] in benzene were degassed, saturated with prepurified nitrogen (1 atm), and measured using 2-cm quartz cells ($E_{\max}$ ca. ±0.02 kK; $a_{\max}$ ca. ± 2%). All absorption maxima have been found to obey Beer's law. (b) The spectra of the complexes in the microcrystalline state were measured as suspensions in Nujol on filter paper vs. Nujol on filter paper ($E_{\max}$ ca. ±0.1 kK). The infrared spectra (Table V) were recorded on a Beckman IR-12 spectrophotometer (ν ca. ±0.5 cm^{-1}); chloroform or chlorobenzene solutions of oxygen-sensitive compounds were prepared as above and measured in NaCl or Irtran-2 cells.

The kinetic measurements of the oxygenation, hydrogenation, and hydrochlorination of *trans*-[IrCl(CO)L$_2$] (Table VI) were carried out by methods detailed elsewhere.[17,18] The data for some of these reactions have been cited previously.[4,5] Spectral grade solvents were used in all spectroscopic and dynamic experiments.

Chemical Behavior of *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$]. (a) Reaction with Silver Perchlorate.[19] AgClO$_4$ (0.0645 g) and *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] (0.236 g, Ag:Ir = 1) were dissolved in benzene (25 ml) and the mixture was stirred under N$_2$ at 25° for 1 hr. The resulting suspension of AgCl in a yellow solution was filtered directly into hexane (200 ml) which produced a yellow precipitate of *trans*-[Ir(OClO$_3$)(CO)(*o*-tol)$_3$P)$_2$] in 0.145-g (52%) yield. The complex is soluble in benzene, chloroform, and ethanol and insoluble in hexane. The infrared spectrum in Nujol showed these bands: ν_{CO} 1982 (vs); ν_{Ir-CO} 597 (m); ν_{OClO_3} 1160 (m), 1100 (m, b), 1070 (w), 620 (ms) cm^{-1}; and those of coordinated (*o*-tol)$_3$P.

(b) Reactions with Hydrogen Chloride, Hydrogen Bromide, and Bromine. Hydrogen Chloride. A suspension of *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] (0.081 g) in hexane (40 ml), saturated with HCl (1 atm), was stirred at 25° for 17 hr. The product consisted essentially of the starting material, but ca. 5% conversion to [(H)(Cl)IrCl(CO)((*o*-tol)$_3$P)$_2$] was detected. In benzene solution, however, the reaction is complete within a few minutes. On longer exposures to HCl in solution, a further reaction of the hydrido–chloro complex takes place. A solution-suspension of *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] (0.114 g) in benzene (40 ml) was saturated with HCl (1 atm) at 25°. The yellow color of the complex faded within minutes and a clear colorless solution resulted which was stirred for 18 hr during which time a precipitate developed. Hexane (200 ml) was added to this mixture and 0.096 g of a cream-colored product was obtained which consisted of ca. 15% of [(H)(Cl)IrCl(CO)((*o*-tol)$_3$P)$_2$] and 85% of [(Cl)$_2$IrCl(CO)((*o*-tol)$_3$P)$_2$].

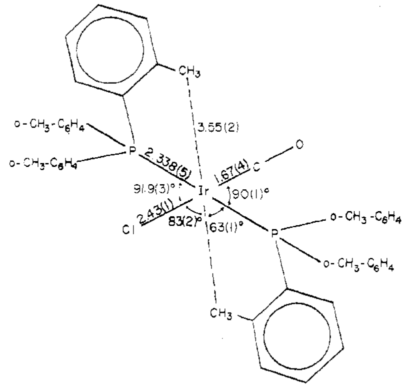

Figure 2. Simplified two-dimensional diagram of the coordination sphere of iridium in *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] showing an approximate arrangement of two ortho CH$_3$ groups in relation to the central atom. See Figure 3 and text for geometric details of the ortho CH$_3$–Ir unit.

Hydrogen Bromide. With this reagent, the results were analogous to those cited above. That is, no reaction was observed between the solid Ir(I) complex and gaseous HBr (1 atm, 25°, 12 hr). In benzene solution, a 0.5-hr exposure to hydrogen bromide (1 atm, 25°) gave a mixture of [(H)(Br)IrCl(CO)((*o*-tol)$_3$P)$_2$] (ca. 40%), [(Br)$_2$IrCl(CO)((*o*-tol)$_3$P)$_2$] (ca. 60%), and a trace of the starting material. After 12 hr (same conditions), a complete conversion to [(Br)$_2$IrCl(CO)((*o*-tol)$_3$P)$_2$] occurred.

Bromine. *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] (0.156 g) in benzene (20 ml) was treated with Br$_2$ (0.2 ml) and a yellow-orange precipitate formed immediately. Hexane (150 ml) was added, the mixture stirred (5 min), and the solid product recrystallized by dissolving it in CHCl$_3$ (15 ml) and reprecipitating with hexane (100 ml); 0.144 g (78%) of [(Br)$_2$IrCl(CO)((*o*-tol)$_3$P)$_2$] was obtained.

All products of the reactions with HCl, HBr, and Br$_2$ were characterized by their infrared spectra (Table VII).

(c) Attempted Reactions. See eq 2–5 and Table VI.

Results

Crystal and Molecular Structure of *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$]. Table II shows the final atomic positional and thermal parameters. Selected bond lengths and angles are given in Table III. Figures 1–3 depict various views of the molecular structure of the complex. All interatomic distances and angles compare favorably with those of similar compounds (except for the environment around the ortho CH$_3$ group, C(8), Figure 3, described below). Other than the Ir–C(8) distance, no unusual intramolecular contacts were found. All intermolecular contacts appear normal.

As expected, the formal coordination about the central atom is square planar (Figure 1) with all the adjacent ligand–Ir–ligand angles close to the theoretical value of 90°. Because there are only two molecules in the unit cell, the Ir atom must

Table I. Crystal Data for *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] (at 25°)

$C_{43}H_{42}P_2OClIr$ fw: 864.4
Crystal habit: prismatic *a*, yellow, from $CHCl_3$–C_6H_6
Crystal dimensions: 0.210 × 0.075 × 0.111 mm, bounded by pinacoidal planes
Unit cell: monoclinic, $P2_1/n$ ($C_{2h}{}^5$, an alternative setting of $P2_1/c$ with general equivalent positions $\pm(x, y, z; {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$), absent spectra $0k0$ for $k = 2n + 1$, $h0l$ for $h + l = 2n + 1$; $a = 15.689$ (6) Å, $b = 10.981$ (3) Å, $c = 10.739$ (4) Å, $\beta = 92.93$ (3)°, $V = 1848$ (2) Å^3, $Z = 2$, $d_{\text{calcd}} = 1.554$ (2) g/cm^3, $d_{\text{found}} = 1.7$ (2) g/cm^3, $F(000) = 864.0$
Radiation: Mo Kα, λ 0.71069 Å, Nb filtered; $\mu_{\text{Mo K}\alpha} = 40.2$ cm^{-1}

Experimental Data

Cell dimensions: least-squares refinement of 2θ value for 13 reflections, $2\theta_{\text{min}} = 4.5°$, $2\theta_{\text{max}} = 18.9°$; 2θ values calculated from measurements of 4θ at 1° takeoff angle
Intensities: measured by stationary-crystal, stationary-counter method, counting time 20 sec, 2 peak and 2 background measurements per reflection, measurements made to $2\theta_{\text{max}} = 40°$ for all reflections (including systematic absences) in a full hemisphere, equivalent net intensities averaged with agreement generally within 5%, number of measurements 4200, unique reflections (excluding systematic absences) 1823, observed 1230, unobserved 593 at 99% confidence, observations/parameters = 10.5
Corrections: (1) crystal decomposition based on 2 standard reflections, (2) conversion of peak height measurements to integrated intensities by the equation (integrated intensity)/(peak intensity) = $4.3459 - 6.7046 \tan^2 \theta$, developed from a least-squares treatment of measured ratios for 19 strong reflections;[9] (3) $1/Lp$
Structure determination: Ir fixed at 0, 0, 0 by symmetry, P located from three-dimensional Patterson, other atoms located from successive difference electron density maps
Refinement: by full-matrix least squares, minimizing $\Sigma w(\Delta F)^2$, where $w^{1/2} = |F_o|/44.5$ for $|F_o| < 44.5$, $44.5/|F_o|$ for $|F_o| \geqslant 44.5$, $12.7 < |F_o| < 287.7$, unobserved reflections excluded, mean and maximum shift/esd = 0.2 and 1.7, respectively, in final cycle, Ir, P, and Cl refined anisotropically, C and O isotropically; C(1) and O temperature factors fixed in final cycle
Final agreement: $R = 0.047$ for observed reflections, $|F_c| \leqslant |F_o|$ for 587 unobserved reflections, $|F_o| < |F_c| \leqslant 1.5|F_o|$ for 6 unobserved reflections; $R_w = 0.055$ for all the observed reflections
Residual electron density: $|\Delta\rho| < 1.0$, $\sigma(\rho) = 0.3$ e/Å^3
f curves: analytic scattering factors[10] used, with Ir corrected for anomalous dispersion ($\Delta f' = -1.80$, $\Delta f'' = 9.0$)[11]
Computer programs: intensity data processing, **DATCO4**;[12] data reduction, **NRC-2**;[13] full-matrix least-squares refinement, **LSREF**;[14] Fourier maps, **FORDAP**;[15] bond lengths, angles, and mean planes, **NRC-12** and **NRC-22**;[13] stereodrawings, **ORTEP-II**[16]
Diffractometer: General Electric XRD-6 with Datex automation

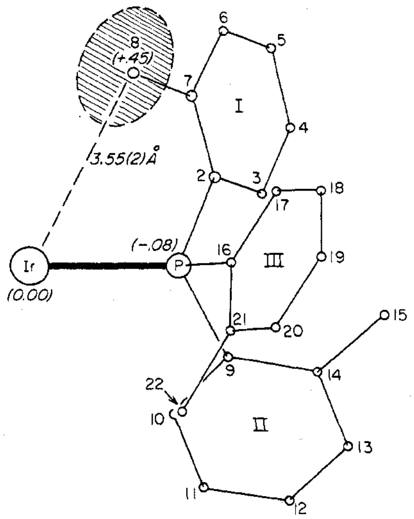

Figure 3. View of a section of *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] along the Cl–Ir–CO axis which is perpendicular to the plane of the paper. Phenyl rings I, II, and III of the (o-$CH_3C_6H_4$)$_3$P ligand form dihedral angles of 56.7, 29.0, and 63.2°, respectively, with the plane of paper. The figures in parentheses near Ir, P, and C(8) show the distance (in Å) of the atom above (+) or below (−) the paper. The C(7)–C(8) bond forms an angle of ca. 50° with the plane of paper. The hydrogen atoms of the C(8) methyl group (not located from the X-ray data) would be expected to be projected on the shaded area extending from C(8) (based on ideal geometry, C–H = 1.05 Å, H–C–H = 109°).

lie at a center of symmetry. Consequently, both the chloro and carbonyl ligands must be randomly disordered. Careful measurements of the systematically absent reflections did not provide any evidence for a lower symmetry which would permit an ordered structure. Similar examples of disorder between coordinated halogen and carbon monoxide have been reported.[20] Thus, the present model is not unreasonable. It was possible, however, to resolve the atoms comprising the carbonyl ligand successfully, probably because of their relatively low thermal motion.

In the early cycles of refinement, no attempt was made to locate the carbonyl group. The model assumed that the Cl site was half-occupied as required by the space group symmetry. A difference electron density map made after locating all other atoms showed two clearly resolved peaks corresponding to the CO group. The positional and thermal parameters of the chloro and carbonyl ligands were fixed in alternate cycles because of excessive correlation between these atoms. In the final cycle, only the isotropic temperature factors of the carbonyl group were fixed. Thus, the estimated standard deviations reported in Table II for the *B* values for C(1) and

Table II. Final Atomic Positional and Thermal Parameters[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Ir	0	0	0	540 (6)	508 (6)	409 (5)	17 (8)	63 (3)	−4 (9)
P	1045 (3)	1162 (4)	−924 (4)	522 (29)	519 (29)	404 (25)	41 (23)	9 (20)	2 (25)
Cl	−306 (9)	1631 (11)	1440 (14)	598 (66)	696 (105)	570 (71)	−7 (62)	156 (54)	6 (71)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
O	365 (41)	−1985 (57)	−1602 (58)	10.3 (1.0)	C(12)	3733 (13)	−491 (19)	−433 (19)	5.8 (0.5)
C(1)	189 (28)	−1163 (40)	−955 (38)	4.2 (0.7)	C(13)	3677 (13)	646 (20)	−989 (18)	5.8 (0.5)
C(2)	785 (10)	1272 (16)	−2600 (14)	3.8 (0.3)	C(14)	2861 (10)	1213 (17)	−1182 (15)	4.2 (0.4)
C(3)	1383 (11)	796 (17)	−3426 (16)	4.8 (0.4)	C(15)	2856 (11)	2463 (18)	−1780 (16)	5.4 (0.4)
C(4)	1207 (12)	837 (19)	−4739 (17)	5.6 (0.4)	C(16)	1182 (10)	2704 (16)	−316 (15)	4.2 (0.4)
C(5)	468 (13)	1331 (20)	−5209 (19)	6.2 (0.5)	C(17)	961 (11)	3685 (18)	−1110 (16)	4.9 (0.4)
C(6)	−133 (12)	1765 (19)	−4422 (18)	5.6 (0.4)	C(18)	1089 (12)	4888 (25)	−647 (18)	7.0 (0.5)
C(7)	−2 (11)	1738 (18)	−3078 (16)	4.9 (0.4)	C(19)	1458 (12)	5123 (25)	535 (18)	6.8 (0.5)
C(8)	−720 (13)	2174 (20)	−2263 (18)	6.5 (0.5)	C(20)	1689 (13)	4102 (20)	1291 (18)	6.1 (0.5)
C(9)	2132 (11)	562 (17)	−783 (16)	4.4 (0.4)	C(21)	1558 (11)	2918 (18)	887 (17)	5.2 (0.4)
C(10)	2228 (12)	−593 (18)	−249 (17)	4.8 (0.4)	C(22)	1836 (11)	1869 (18)	1763 (17)	5.4 (0.4)
C(11)	3052 (12)	−1129 (19)	−49 (17)	5.8 (0.4)					

[a] C(1) and O comprise the carbonyl ligand (Figure 2); for the numbering scheme of other carbon atoms, sce Figure 3; x, y, and z are multiplied by 10^4, and U_{ij}, by 10^3; the anisotropic thermal correction is of the form $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2klb^*c^*U_{23} + \ldots]$.

Table III. Selected Interatomic Distances (Å) and Angles (deg) in *trans*-$[IrCl(CO)((o\text{-}tol)_3P)_2]$[a]

Distances

Ir-P	2.338 (5)	P-C(9)	1.83 (2)
Ir-Cl	2.43 (1)	P-C(16)	1.82 (2)
Ir-C(1)	1.67 (4)	C(7)-C(8)	1.54 (3)
C(1)-O	1.18 (8)	C(14)-C(15)	1.52 (3)
P-C(2)	1.83 (2)	C(21)-C(22)	1.54 (3)

Summary of C-C Distances in Phenyl Rings

Mean	1.41	Std dev	0.03
Min	1.35 (3)	Av esd	0.03
Max	1.45 (3)		

Angles

P-Ir-Cl	91.9 (3)	C(9)-P-C(16)	102.3 (8)
P-Ir-C(1)	90 (1)	Ir-C(1)-O	177 (5)
Cl-Ir-C(1)	178 (2)	C(2)-C(7)-C(8)	124 (2)
Ir-P-C(2)	109.2 (5)	C(6)-C(7)-C(8)	119 (2)
Ir-P-C(9)	116.1 (6)	C(9)-C(14)-C(15)	126 (2)
Ir-P-C(16)	115.3 (6)	C(13)-C(14)-C(15)	116 (2)
C(2)-P-C(9)	105.3 (8)	C(16)-C(21)-C(22)	122 (2)
C(2)-P-C(16)	107.9 (8)	C(20)-C(21)-C(22)	119 (2)

Summary of C-C-C angles in Phenyl Rings

Mean	120	Std dev	2
Min	117 (2)	Av esd	2
Max	124 (2)		

[a] C(1) and O comprise the carbonyl ligand (Figure 2); for the numbering scheme of the other carbon atoms, see Figure 3.

Table IV. Planarity of Phenyl Rings and Ortho Tolyl Groups in $(o\text{-}tol)_3P$ Ligand[a]

	Phenyl ring and atoms		
	I, C(2)-C(7)	II, C(9)-C(14)	III, C(16)-C(21)
Max dist from mean plane, Å	0.02	0.01	0.01
Av esd	0.02	0.02	0.02
χ^2	2.72	0.82	1.67
Dist of methyl carbon from plane, Å	−0.11 (2)	−0.01 (2)	0.02 (2)
Dist of Ir from plane, Å	−1.914	−0.297	−1.861

[a] For atom-numbering scheme, see Figure 3.

O are derived from the next to last cycle of refinement. Analysis of the thermal anisotropy of the Cl showed that the orientation of the principal axis of the thermal ellipsoid differed considerably from the Ir–Cl direction. Therefore, these parameters would seem to be unaffected by the disorder problem.

One of the ortho methyl carbon atoms, C(8) (Figure 3), is located above and another, by symmetry, below the coordination plane (not shown in Figure 3; see Figures 1 and 2). The C(8)–Ir distance, 3.55 (2) Å, is somewhat short for a nonbonded interaction, and the Ir–C(8) direction (broken line in Figure 3) forms an angle of 28.7° with the normal to the *trans*-$IrCl(CO)P_2$ plane. The angles P–Ir–C(8) and Cl–Ir–C(8) are 63 (1) and 83 (2)°, respectively. Unlike the ortho carbons of the other two tolyl groups (C(15) and C(22), Figure 3), which are coplanar with their respective phenyl rings (Table IV), C(8) is significantly out of the plane, 0.11 Å, in the direction of the iridium atom.

Spectral, Dynamic, and Chemical Data. Table V shows the infrared and electronic spectral data for *trans*-$[IrCl(CO)((o\text{-}tol)_3P)_2]$ and some related complexes. A comparison of the reactivities of these compounds toward O_2, H_2, and HCl and the stabilities of the resulting Ir(III) complexes is given in Table VI.

Equations 2–8 (L = $(o\text{-}tol)_3P$) summarize the chemical

$$\begin{array}{llr}
\textit{trans}\text{-}[IrCl(CO)L_2] + SO_2 & \rightarrow NR\ ([(SO_2)IrCl(CO)L_2]) & (2)\\
\quad + C_2(CN)_4 \text{ (or related } C_2R_4) & \rightarrow NR\ ([(C_2(CN)_4)IrCl(CO)L_2]) & (3)\\
\quad + NaBH_4 & \rightarrow NR\ ([IrH_3(CO)L_2]?) & (4a)\\
\quad + NaBH_4 + L & \rightarrow NR\ ([IrH(CO)L_3]?) & (4b)\\
\quad + N_2H_4 & \rightarrow NR\ ([IrH(CO)L_3]?) & (5a)\\
\quad + N_2H_4 + L & \rightarrow NR\ ([IrH(CO)L_3]?) & (5b)
\end{array}$$

$$\textit{trans}\text{-}[IrCl(CO)L_2] \xrightarrow{+HX} [(H)(X)IrCl(CO)L_2] \xrightarrow[-H_2]{+HX} [(X)_2IrCl(CO)L_2] \qquad (6)$$

X = Cl or Br

$$\textit{trans}\text{-}[IrCl(CO)L_2] + Br_2 \rightarrow [(Br)_2IrCl(CO)L_2] \qquad (7)$$

$$\textit{trans}\text{-}[IrCl(CO)L_2] + AgClO_4 \rightarrow [Ir(OClO_3)(CO)L_2] + AgCl \qquad (8)$$

behavior of the title compound at room temperature. When no reaction (NR) was observed, the formula of the expected product, by analogy with the well-established chemistry of *trans*-$[IrCl(CO)(Ph_3P)_2]$, is given in parentheses. (For the expected addition compounds with O_2 and H_2, see Table VI.)

The experiments with sulfur dioxide (p_{SO_2} = 700 mm; C_6H_6; 12 hr; eq 2) and substituted π-acceptor olefins (excess; C_6H_6; several hours; eq 3) represent our standard tests for the basicity and coordination unsaturation of low-valent metal complexes. The main objective for the attempted reactions with $NaBH_4$ and N_2H_4 (excess; C_2H_5OH; 1 week; eq 4, 5) was to synthesize $[IrH(CO)L_2]$, in hope that the steric properties of the $(o\text{-}tol)_3P$ ligand might prohibit the formation of the trisphosphine derivative $[IrH(CO)L_3]$,[21] which invariably results under these conditions (eq 4b, 5) when L is Ph_3P.[22] The four-coordinated iridium(I)–hydrido complex still appears to be elusive (i.e., not isolated in pure state), although there is substantial evidence for its existence as an intermediate in various reactions.[17]

The reactions with hydrogen halides and the resulting products (eq 6, 7) are of the familiar types originally observed with the model compound *trans*-$[IrCl(CO)(Ph_3P)_2]$.[6,23] The infrared spectral data in Table VII are in agreement with the formulation of the complexes as shown.[24] Metal–perchlorato covalent bonds are not commonplace, but the formation and properties of $[Ir(OClO_3)(CO)((o\text{-}tol)_3P)_2]$ (eq 8) are strictly anlogous with those of its congener $[Ir(OClO_3)(CO)(Ph_3P)_2]$.[19]

Table V. Vibrational and Electronic Spectral Data for *trans*-$[IrCl(CO)L_2]$

	Infrared spectral data,[a] cm^{-1}				Electronic spectral data, E_{max},[b,c] kK					
	ν_{CO}		ν_{Ir-CO}	ν_{IrCl}	Benzene soln			Crystals in Nujol		
L	Nujol	$CHCl_3$	Nujol	Nujol						
$(C_6H_5)_3P$	1954	1965	604	321	22.8 (730)	25.8 (4040)	29.5 (3160)	22.8	25.8	29.5
$(p\text{-}CH_3C_6H_4)_3P$	1956	1962	611	314	22.7 (680)	26.0 (3670)	29.5 (2950)	22.7	25.7	30.0
$(m\text{-}CH_3C_6H_4)_3P$	1955	1964	603	315	22.7 (740)	25.9 (4080)	29.5 (3120)	22.7	25.6	29.8
$(o\text{-}CH_3C_6H_4)_3P$	1948	1960	603	315	23.9 (580)	26.6 (2540)	30.4 (2790)	23.9	26.9	30.9
$(C_6H_{11})_3P$	1934	1931[d]	611	310	23.2 (680)	26.4 (3490)	29.7 (2430)	23.1	26.4	29.8

[a] Intensities: ν_{CO}, vs; ν_{Ir-CO}, ms; ν_{Ir-Cl}, m. [b] Molar absorptivities, a_{max}, M^{-1} cm^{-1}, given in parentheses. [c] All compounds show an additional absorption band >30 kK (ca. 8000 M^{-1} cm^{-1}). [d] In C_6H_5Cl.

Table VI. Rate and Equilibrium Data for Oxygenation, Hydrogenation, and Hydrochlorination of *trans*-$[IrCl(CO)L_2]$ in Chlorobenzene at 30° $(K_2 = k_2/k_{-1})$

$$trans\text{-}[IrCl(CO)L_2] + XY \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} [(XY)IrCl(CO)L_2]$$

L	XY	k_2, $sec^{-1}\ M^{-1}$	$10^{-3}K_2, M^{-1}$
$(C_6H_5)_3P$	O_2	0.059	28
	H_2	1.2	31
	HCl^a	29,000	
$(p\text{-}CH_3C_6H_4)_3P$	O_2	0.096	21
	H_2	1.7	44
	HCl^b	24,000	
$(m\text{-}CH_3C_6H_4)_3P$	O_2	0.044	7.0
	H_2	0.69	25
	HCl^b	2,700	
$(o\text{-}CH_3C_6H_4)_3P$	O_2	No reaction (p_{O_2} 700 mm; 18 days)	
	H_2	No reaction (p_{H_2} 740 mm; 3 hr)	
	HCl^b	0.79	
$(C_6H_{11})_3P$	$O_2{}^c$	0.00038	0.066
	$H_2{}^c$	0.0066	2.4
	HCl^b	≤ 4.0	

[a] k_2(in benzene) = 11,000. [b] Measured in benzene; k_2 ± 10%. [c] 40°.

Table VII. Infrared Spectral Data (cm^{-1}) for Hydrido and Halogeno Complexes of Tervalent Iridium Measured in Nujol[a]

Complex	ν_{IrH}	ν_{CO}
$[(H)(Cl)IrCl(CO)(Ph_3P)_2]$	2240	2024
$[(H)(Cl)IrCl(CO)((p\text{-}tol)_3P)_2]$	2194	2029
$[(H)(Cl)IrCl(CO)((m\text{-}tol)_3P)_2]$	2225	2035
$[(H)(Cl)IrCl(CO)((o\text{-}tol)_3P)_2]$	2195	2033
$[(H)(Cl)IrCl(CO)((C_6H_{11})_3P)_2]$	2209	2012
$[(H)(Br)IrCl(CO)(Ph_3P)_2]$	2240	2022
$[(H)(Br)IrCl(CO)((o\text{-}tol)_3P)_2]$		2032
$[(Cl)_2IrCl(CO)(Ph_3P)_2]$		2075
$[(Cl)_2IrCl(CO)((o\text{-}tol)_3P)_2]$		2060
$[(Br)_2IrCl(CO)(Ph_3P)_2]$		2072
$[(Br)_2IrCl(CO)((o\text{-}tol)_3P)_2]$		2060

[a] Intensities: ν_{CO}, vs; ν_{IrH}, m–w. With hydrogen halides, the $(o\text{-}tol)_3P$ complex was only partially converted to the respective hydrido species (see Experimental Section); thus, the ν_{IrH} was either weak or not clearly detectable.

Discussion

According to the infrared and visible spectral data (Table V), the three tritolylphosphine complexes have similar electronic properties. Furthermore, the spectra of the triphenylphosphine and tricyclohexylphosphine derivatives, which are included for comparison, are not essentially different from those of the $(tol)_3P$ compounds. The carbonyl stretching frequency (ν_{CO}) in this type of complex has been interpreted as reflecting the "latent basicity" of *trans*-$[IrCl(CO)L_2]$,[25] or the π-acceptor properties of the tertiary phosphine ligand,[26] and an approximate correlation has been found between the ν_{CO} and the reactivity of *some* of these iridium compounds toward dihydrogen[5,17] and dioxygen:[4,18] the lower the ν_{CO}, the higher the reaction rate.

The lowest energy absorption band in the electronic spectra (Table V) has recently been assigned to a metal-to-ligand charge-transfer transition,[27] and the energy of this absorption has also been observed to be related to the dynamics of some of these addition reactions: the lower the E_{max}, the higher the reactivity of the complex. This correlation seems to hold for series of complexes with strictly isostructural ligands[28] but only approximately or with notable exceptions for others.[4,5,17,18,22]

Thus, as a first approximation, the five complexes listed in Table V would be expected to show not substantially different reactivities as far as their *electronic* dispositions are concerned. Or, considering the cited uncertainties in the spectra–reactivity correlations, the differences in the rate constants should probably not exceed an order of magnitude. The dynamic data summarized in Table VI show, however, that *trans*-$[IrCl(CO)((o\text{-}tol)_3P)_2]$ stands out as a striking exception to these expectations. The reason for its inertness obviously derives from the steric properties of the $(o\text{-}tol)_3P$ ligand and the particular conformation of the two methyl groups relative to the central atom as shown by the structure of the complex (Figures 2, 3).

The small reactivity differences between the triphenyl- and tri-*p*-tolylphosphine complexes are consistent with the reactivity–spectra correlations mentioned previously. This indicates, as expected, that the para CH_3 groups in the $(p\text{-}tol)_3P$ ligand play no steric role relative to para hydrogens in Ph_3P in these addition reactions. This conclusion is also clearly evident from the linear free energy relationships (LFER) for the reactions of these complexes with dihydrogen,[5] dioxygen,[4] and hydrogen chloride.[29] The rate constants for the reactions of the tri-*m*-tolylphosphine compound are only slightly smaller than those found for the Ph_3P and $(p\text{-}tol)_3P$ complexes, in general agreement with predictions based on spectral data. This implies that possible steric hindrance from the meta substituent is not very significant which is again evident from the LFER for these reactions.[5,29] The importance of LFER in assessing the relative magnitude of steric effects in this type of reaction should be emphasized in this context. For example, when L is $(C_6H_{11})_3P$, the second-order rate constants (k_2) for oxygenation, hydrogenation, and hydrochlorination are a few orders of magnitude smaller than those for the corresponding reactions of the triphenylphosphine complex, although such a large difference cannot be due to the electronic properties of the two compounds (Table V). The LFER for these reactions show a very substantial deviation of the tricyclohexylphosphine complex from the linear relationships between the other complexes.[4,5]

Steric effects on the reactivity of the tertiary phosphine (R_3P) complexes under discussion and the stability of their addition compounds with small molecules seem to be related to the rotations of both the R–P and P–Ir bonds during the reaction. Although the phosphines in *trans*-$[IrCl(CO)(R_3P)_2]$ remain in trans positions in $[(XY)IrCl(CO)(R_3P)_2]$ ($XY = H_2, O_2, HCl$), molecular models suggest that the conformations of the R's in the products differ from those in the starting material, a change which would require activation energy, its magnitude depending on the particular tertiary phosphine. On the basis of the steric properties of the R groups, we would predict the rotational energies of the phenyl and para tolyl fragments in the Ph_3P and $(p\text{-}tol)_3P$ ligands, respectively, to be nearly identical and those of the meta tolyl groups in $(m\text{-}tol)_3P$ to be only slightly more restricted, in agreement with the LFER data cited above. For the tricyclohexylphosphine complex, however, full rotation of both the chair and boat forms of the C_6H_{11} ring seems prohibited, and only very small conformational changes are possible according to models, although the twist form exhibits a somewhat freer rotation.

The molecular model of *trans*-$[IrCl(CO)((o\text{-}tol)_3P)_2]$ shows, as expected, that rotations of the ortho tolyl groups are greatly more hindered than those in the other tolylphosphine ligands, but these restrictions are less pronounced than in the tricyclohexylphosphine complex which reacts measurably (although slowly and incompletely) with H_2 and O_2 under mild conditions while *trans*-$[IrCl(CO)((o\text{-}tol)_3P)_2]$ does not. This apparent discrepancy can be explained by noting one important difference in the structural features of the two compounds according to models and the experimentally determined molecular structure of the $(o\text{-}tol)_3P$ complex in which two of the ortho carbons are relatively close to the central atom (Figures 2, 3). The Ir–C distance, 3.55 Å, *and* the observation that this carbon atom is significantly out of the plane of the phenyl ring (0.11 Å) to which it is bonded (in contrast to the normal planar geometries of the two other ortho tolyl groups of the same ligand) strongly imply some interaction between the methyl hydrogen(s) and the iridium atom [C:H$^{\delta+}$---$^{\delta-}$:Ir(filled d_{z^2} orbital)]. This apparent interaction seems to be responsible for locking the two *o*-CH_3 groups into the conformation observed and probably adds substantially to the total energy barrier of rotation. In any case, the two nearly apical methyls in *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] block the approach of the addendum (H_2, O_2, SO_2, etc.) to the central atom and they must move from these positions in order that an addition reaction can occur.

The situation in *trans*-[IrCl(CO)((C_6H_{11})$_3$P)$_2$] is quite different in these respects. Although conformations of the cyclohexyl groups can be constructed which permit a relatively close approach of the ortho hydrogens to iridium, these Ir–H_2C distances are considerably longer than in the (*o*-tol)$_3$P complex, and, furthermore, the hydrogen atoms in question are far from the apical positions; i.e., they approach Ir sideways.

Returning to the structure–reactivity problem of *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$], the question arises about the relationship between the configuration in the solid state, discussed thus far, and that in solution where the reactions have been tested. The near identity of the electronic spectra in both media (Table V) suggests that the essential features of the conformation found in the crystal prevail also in solution, and the relative inertness of the complex (Table VI) supports this premise. The infrared spectra (ν_{CO}) of the solid and dissolved compound show some difference, but the ν_{CO} shift is not large and common to all complexes of this type (Table V). The spectral data of *trans*-[IrCl(CO)((*o*-tol)$_3$P)$_2$] also give unambiguous evidence that this compound is best formulated as a formally *uni*valent and *four*-coordinated iridium complex (cf. ref 2c and Tables V, VII), the observed apical Ir–H_3C contacts notwithstanding.

As shown by eq 6 and 7 and the data in Table VII, the (*o*-tol)$_3$P complex reacts with hydrogen halides and halogens to form apparently genuine six-coordinated complexes of tervalent iridium, by analogy with the normal behavior of *trans*-[IrCl(CO)L_2] (L = sterically unobstructed tertiary phosphine). The general addition reactions of these complexes (eq 1) have been interpreted as acid–base or oxidation–reduction processes,[2c,6,23,25] and hydrogen halides (HX) and halogens (X_2) are strong acids; they stand at the extreme end of the acidity sequence of XY relative to *trans*-[IrCl(CO)-(Ph_3P)$_2$]. The latter and related species react instantaneously with gaseous HX even in the solid state.[22,24] The rates of the additions of HX to the (*o*-tol)$_3$P complex are greatly lower (Experimental Section, Table VI). But the fact that these reactions are observed shows that the strong acids overcome the total rotational barrier in the complex. It should be added in this context that molecular models indicate that six-coordinated [(XY)IrCl(CO)((*o*-tol)$_3$P)$_2$] with XY = HX, X_2, H_2, and O_2 are all structurally feasible. Thus, the observed inertness toward dihydrogen and dioxygen appears to derive from the high activation energies of these potential reactions rather than from exclusive steric properties of the (*o*-tol)$_3$P ligand.

The stereochemical characteristics of the tertiary phosphines discussed in this article do not seem to affect the planar symmetry of the four-coordinated IrCl(CO)P_2 core (at least as far as the title compound is concerned, but this may not be true for others, e.g., the (C_6H_{11})$_3$P derivative). There is an interesting example, however, which shows an experimentally established tetrahedral distortion from planarity of an ML_4 unit, [Ir(CH_3(C_6H_5)$_2$P)$_4$]$^+$.[30] This d^8 complex does not react with molecular oxygen or carbon monoxide, but its inertness appears to result from a decreased availability of appropriate metal d orbitals for interacting with the potential addenda (O_2, CO). This electronic effect is considered to derive from the geometric ML_4 distortion caused by the particular conformation of the ligands. An extreme case in the same direction, i.e., where a "complete" interweaving of electronic and stereochemical properties of a four-coordinated d^8 complex seems to render it inactive, is represented by [CoCl(Ph_3P)$_3$].[31] This compound is reportedly tetrahedral (as suggested by magnetic and spectral evidence) which is rather unusual for a d^8 ML_4 complex, but the configuration may be explained by observing that the *three* large triphenylphosphine ligands cannot be readily accommodated in a planar manner around the relatively small cobalt atom. [CoCl(Ph_3P)$_3$] does not measurably react with H_2 or O_2 under ordinary conditions,[32] while its planar analogs, [Co(PC_2P)$_2$]$^+$ and [Co(PC=CP)$_2$]$^+$,[33] display very high rates of reaction with these molecules.[28b]

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Registry No. *trans*-[IrCl(CO)((C_6H_5)$_3$P)$_2$], 15318-31-7; *trans*-[IrCl(CO)((*p*-$CH_3C_6H_4$)$_3$P)$_2$], 28195-56-4; *trans*-[IrCl-(CO)((*m*-$CH_3C_6H_4$)$_3$P)$_2$], 34054-06-3; *trans*-[IrCl(CO)((*o*-$CH_3C_6H_4$)$_3$P)$_2$], 56487-57-1; *trans*-[IrCl(CO)((C_6H_{11})$_3$P)$_2$], 34054-07-4; *trans*-[Ir($OClO_3$)(CO)((*o*-$CH_3C_6H_4$)$_3$P)$_2$], 56453-90-8; $AgClO_4$, 7783-93-9; O_2, 7782-44-7; H_2, 1333-74-0; HCl, 7647-01-0; HBr, 10035-10-6; Br_2, 7726-95-6.

Supplementary Material Available. A listing of structure factors based on the parameters shown in Table II and showing h, k, l, $10|F_o|$, and $10|F_c|$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50338W-11-75.

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Examination of Photophysics in Rare Earth Chelates by Laser-Excited Luminescence

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We report time-resolved and spectrally resolved luminescence investigations for several chelates of Eu(III) and Tb(III) as well as for the Eu^{2+} ion in glass-forming solvents. For those Eu(III) chelates in which the lowest ligand triplet state lies above the $^5D_1$ term of Eu(III), luminescence is observed from both $^5D_1$ and $^5D_0$. The $^5D_1$ level is observed to decay exponentially in time, while luminescence from $^5D_0$ shows a rapid rise followed by a slower rise and then a very slow decay. The characteristics of these luminescence decays are examined as a function of ligand, temperature, and solvent. The results are discussed in terms of a simple kinetic scheme. In the Tb(III) complexes studied, no emission other than that from the $^5D_4$ term was observed. It is proposed that ligand singlet–triplet energy transfer can occur by a spin-allowed process involving electronic levels of the rare earth complex. The 200-nsec lifetime of emission from Eu^{2+} near 4020 Å suggests that an interconfigurational transition may be involved.

I. Introduction

The mechanisms by which electronic energy, initially fed into spin-allowed absorption bands of numerous rare earth complexes, is funnelled into luminescing states, often with high efficiency, have been the subjects of extensive experimental and theoretical investigation. Understanding energy transfer in rare earth complexes is of immediate interest both to the fundamental theory of inorganic photophysical processes and to the very pragmatic development of better rare earth photosensitive and laser materials. In the first instance, rare earth complexes offer the possibility for modification of one part of the molecular system without drastically changing the other part. This opportunity does not exist, for instance, in most transition metal complexes where the ligand field is extremely important for the determination of the energy level structure. In the second instance, if we understand how energy is transferred from the ligand to the ion, we should be able better to predict changes that will yield higher quantum yields and more efficient sensitization.

Our knowledge of the dynamic photophysics of coordination complexes has been largely confined to the radiative and nonradiative processes between the lowest energy excited states and the ground states of the electronic manifolds. The pathways between *different* excited states can be partially mapped by quantum yield studies but little dynamic information has been available for these important processes. Eu(III) chelates demand particular attention in this regard because the steady-state luminescence in some cases arises from two neighboring states in the $4f^6$ configuration, suggesting the possibility for defining explicitly energy-transfer processes directly from the time-resolved emission characteristics of both the initial and terminal states.

In the present work, we have investigated the rates of nonradiative processes involving excited states in some Eu(III) and Tb(III) chelates with the aid of the tunable dye laser. Similar work on some Cr(III) complexes has been reported elsewhere.[1] Some observations of luminescence from the Eu^{2+} ion are reported here also.

A typical energy level diagram for the important electronic states of the Eu(III) chelates studied is shown in Figure 1. The positions of low-energy ligand-centered singlet (S_1) and triplet (T_1) levels vary with the ligand. For Tb(III) the energy level structure is similar, although the energy ordering of levels defined by the subscript J is reversed. The radiative transitions of interest in this work are Laporte forbidden and spin forbidden.[2] The energies of ligand-localized states are, of course, strongly dependent on the ligands.

II. Experimental Section

Piperidinium tetrakis(dibenzoylmethido)europate(III), $[Eu(dbm)_4]Hpip$, tris(8-hydroxyquinolato)europium(III), $[Eu(8\text{-}hq)_3]\cdot H_2O$, tris(acetylacetonato)europium(III), $[Eu(acac)_3]\cdot H_2O$, and piperidinium tetrakis(dibenzoylmethido)terbate(III), $[Tb(dbm)_3]Hpip$, were isolated from ethanolic solutions of anhydrous $EuCl_3$ or $TbCl_3$, piperidine, and the appropriate ligand and were recrystallized. Tris(dibenzoylmethido)europium(III), $[Eu(dbm)_3]$, was formed on high-vacuum pumping of $[Eu(dbm)_4]Hpip$ at 145°C for 36 hr. Tris(dipivaloylmethido)europium(II), $[Eu(thd)_3]$, was obtained from Aldrich Chemical Co. Tris(dipivaloylmethido)(1,10-phenanthroline)europium(III), $[Eu(thd)_3phen]$, was prepared by Dr. F. Kaufman.[3] Tris(acetylacetonato)terbium(III), $[Tb(acac)_3]\cdot H_2O$, was prepared by adapting the method of Lyle and Witts.[4] Elemental analyses confirmed the identity of the complexes obtained.[1a]

The complexes were dissolved in appropriate glass-forming solvents, including (equal parts by volume) diethyl ether–2-methylbutane (EP), diethyl ether–2-methylbutane–ethanol (EPA), methanol–ethanol (ME), and methylcyclohexane–2-methylbutane (MCHIP). Approximately 1-ml samples were filtered through fritted glass and were introduced into 18-mm Pyrex ampoules. These were repeatedly degassed by freeze (77 K)–pump (10^{-6} Torr)–thaw cycles and sealed off. During luminescence experiments, these ampoules were completely