Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. CHE 75-14460) for support of this research.

Registry No. **1**, 12318-88-6; **2**, 62154-28-3; **3**, 67426-08-8.

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Cone Angle and Ligand Profile Calculations for Bulky Phosphine Ligands

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Received March 7, 1978

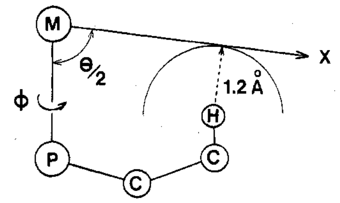

Figure 1. Details of the calculation of the maximum semicone angle, $\theta/2$. The point of contact of the cone-generating vector M → X from the metal, with the van der Waals sphere of the hydrogen atom, is coplanar with the metal, phosphorus, and hydrogen atoms.

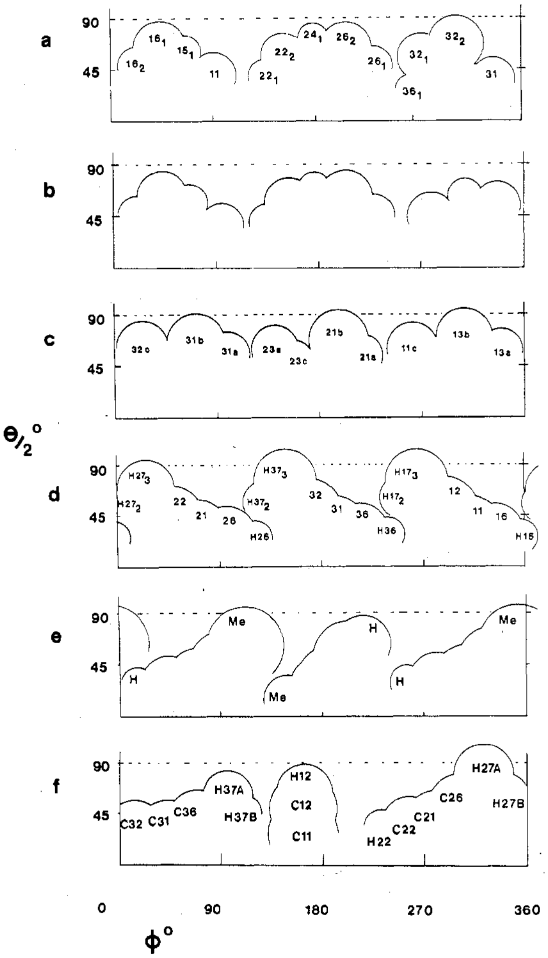

Figure 2. Ligand profiles for (a) Cy_3P in $Cy_3PHg(SCN)_2$; (b) Cy_3P in $(Cy_3P)_3Pt$; (c) t-Bu_3P in t-$Bu_3PHg(OAc)_2$; (d) $(o\text{-tol})_3P$ in $[(o\text{-tol})_3P)HgCl\cdot ClO_4]_2$; (e) $(o\text{-tol})_3P$ in $[(o\text{-tol})_3PHg(OAc)_2]_2$; (f) $(o\text{-tol})_3P$ in $((o\text{-tol})_3P)_2PtI_2$. The ordinate is the maximum semicone angle $\theta/2$. The abscissa is the angle ϕ through which the vector M → X (Figure 1) has been rotated about the M–P bond; the origin of ϕ was arbitrarily chosen. The numbers under some of the curves denote the hydrogen and carbon atoms (Figure 3), whose van der Waals spheres define the ligand profile. For (d), (e), and (f) both carbon and hydrogen atoms define the profile; for (a), (b), and (c) only hydrogen atoms are required.

Various studies[1] showing that the chemistry of metal complexes of tertiary phosphines is markedly affected by the steric effects of the substituents on the phosphorus atom have prompted attempts by Tolman[2] and others[3] to gauge quantitatively the steric requirements of such ligands. On the basis of measurements made from CPK models[4] a ligand cone angle θ was defined[2] to express the bulk of a phosphine ligand. Obtaining maximum cone angles from x-ray data involves the calculation of maximum semicone angles, $\theta/2$ (Figure 1), for each organic moiety of the phosphine ligand from coordinates and van der Waals radii data.[5] A mean $\theta/2$ is then obtained leading to a maximum cone angle θ. Our calculations[6-10] have already shown that Tolman's predictions of θ from models are, for the most part, in good agreement with those actually found. It is also very clear that bulky phosphine ligands do not behave as regular solid cones but are better described as irregular conic cogs. To place these ideas on a quantitative basis we have developed the concept of a "ligand profile"[7] which not only yields precise maximum cone angle data but also provides quantitative information about the gaps between moieties in a ligand—the "depth of tooth" of the conic cog. Immirzi and Musco[11] have also attempted to gain information about the bulk of phosphine ligands by evaluating a solid angle Ω from which they obtain an estimate of what they call $\bar{\theta}$. The $\bar{\theta}$ values so obtained are invariably less than those estimated by Tolman, or calculated by us, and the more cog-like the ligand the greater is the discrepancy. The results of our calculations

Table I. Cone Angle Data[a] for Phosphine Ligands

	max semicone angles $\theta/2$, deg	cone angle θ, deg	θ from models,[1] deg	orientation torsion angle,[b] deg	comments	ref
$[Cy_3PHg(SCN)_2]_n$	86.7, 87.3, 91.9	177	179	63, 170, 87	uncrowded	8
$[Cy_3PHg(NO_3)_2]_2$	89.9, 90.5, 90.9	181	170[15]	65, 172, 95		7
$[Cy_3PHg(OAc)_2]_2$	84.5, 88.9, 95.1	179		63, 177, 86		12
$(Cy_3P)_2Hg(OAc)_2$	83.0, 86.3, 86.9	171		56, 185, 80	crowded	12
	78.5, 85.5, 89.0	170		69, 177, −45		
$(Cy_3P)_2Hg(ClO_4)_2$	79.1, 82.6, 87.2	166		53, 181, −46		12
	78.2, 82.9, 86.2	165		56, 182, −45		
$(Cy_3P)_3Pt$	76.3, 84.3, 85.0	164		71, 175, −42		11
$(Cy_3P)_2PtI_2$	74.9, 84.3, 85.9	163		63, 175, −44		18
t-$Bu_3PHg(OAc)_2$	91.9, 93.9, 95.1	187	182		uncrowded	10
t-$Bu_3PHg_2(SCN)_4$	92.9, 94.2, 96.5	189				12
t-$Bu_3PNiBr_3^-$	88.0, 88.2, 88.2	176			crowded	6
$[(o\text{-tol})_3PHgCl\cdot ClO_4]_2$	93.6, 101.4, 102.0	198	194	128, 128, 127	uncrowded	12
$[(o\text{-tol})_3PHg(OAc)_2]_2$	86.6, 99.7, 99.8	191		32, −125, −121	crowded	12
$((o\text{-tol})_3P)_2PtI_2$	82.8, 88.6, 103.8	183		−1, −106, −119		12
$((o\text{-tol})_3P)_2IrClCO$	84, 89, 102	183		6, −120, −113		21

[a] All cone angles and ligand profiles were calculated using a modification of a molecular geometry program originally supplied by Dr. J. Trotter of the University of British Columbia. [b] The torsion angle refers to the M–P–C–H value for Cy_3P ligands and to the M–P–C–C(H) value for $(o\text{-tol})_3P$ ligands.

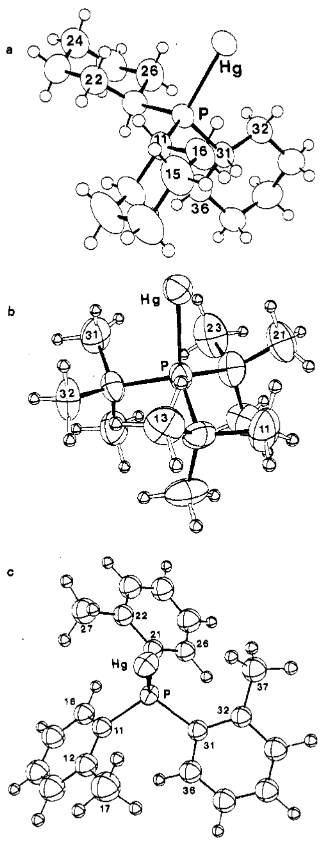

Figure 3. ORTEP view of the Cy_3P, t-Bu_3P, and $(o\text{-tol})_3P$ ligands whose ligand profiles are given in Figures 2a, c, and d.

which yield maximum cone angle data are presented in this paper.

When the vector M → X (Figure 1) is rotated about the M–P bond of a phosphine ligand, just touching the surface of the van der Waals spheres of the atoms of the ligand, the value of $\theta/2$ varies considerably. A "ligand profile" is obtained by plotting the maximum semicone angle, $\theta/2$, as a function of the angle ϕ through which the M → X vector is rotated about the M–P bond, starting from an arbitrary origin. Such a profile is an effective fingerprint in defining the orientation relative to the M–P bond of the groups bonded to phosphorus in bulky phosphine ligands, and we have found it invaluable in comparing the steric requirements of these ligands in a variety of steric environments.

The ligand profiles of uncrowded Cy_3P ligands, as for example $Cy_3PHg(SCN)_2$,[8] $[Cy_3PHg(NO_3)_2]_2$,[7] and $[Cy_3PHg(OAc)_2]_2$,[12] are essentially identical. That for $Cy_3PHg(SCN)_2$ is shown in Figure 2a and a conventional ORTEP[13] view of the ligand is given in Figure 3a. Details of the maximum semicone angles $\theta/2$, cone angles θ, and orientation of the cyclohexyl rings relative to the Hg–P bond (as measured by the Hg–P–C–H torsion angles) are in Table I along with the resultant mean cone angles and those predicted from CPK models.[14] The Cy_3P cone angles in these uncrowded molecules are in the 177–181° range in accord with the value (179°) estimated by Tolman from models.[15] It is noteworthy that in each Cy_3P ligand the same relative orientation of cyclohexyl rings occurs, with Hg–P–C–H torsion angles close to 60, 180, and 90°.

It is well-known that a large cone angle θ does not preclude other bulky ligands from bonding to the central metal. Thus, although the cone angle for uncrowded Cy_3P is close to 180°, derivatives with two and three Cy_3P groups attached to the metal atom are known, e.g., $(Cy_3P)_2CuClO_4$[16] and $(Cy_3P)_3Pt$.[17] Our x-ray studies and calculations show that when the Cy_3P ligand is crowded, the cyclohexyl orientations change (Table I) to decrease the maximum cone angle (e.g., to 163°). Values for $\theta/2$ and θ for $(Cy_3P)_2Hg(ClO_4)_2$,[12] $(Cy_3P)_2Hg(OAc)_2$,[12] $(Cy_3P)_3Pt$,[17] and $(Cy_3P)_2PtI_2$[18] are shown in Table I and are smaller than the original model value.[15] The ligand profiles for these crowded systems are similar to each other but quite different from that found for the uncrowded Cy_3P system; the sole exception is with one of the $(Cy_3P)_2Hg(OAc)_2$ molecules whose profile resembles the uncrowded ones. A typical crowded profile (for $(Cy_3P)_3Pt$) is given in Figure 2b. A 170° cone angle, similar to those reported here for crowded Cy_3P ligands, has also been deduced from spectroscopic studies[3a,3b] under dynamic ligand rotation conditions of the sterically crowded $Cy_3PCo(DH)_2CH_3OH^+$ (where DH = monoanion of dimethylglyoxime).

The ligand profiles for the more bulky t-Bu_3P ligands in the complexes t-$Bu_3PHg(OAc)_2$[10] and t-$Bu_3PHg_2(SCN)_4$[12] are essentially identical; that for t-$Bu_3PHg(OAc)_2$ is shown in Figure 2c and a conventional ORTEP view is shown in Figure 3b. Details of $\theta/2$ and θ are given in Table I. When the t-Bu_3P ligand is crowded as in t-$Bu_3PNiBr_3^-$,[6] the ligand conformation and profile stay substantially as in the previous two examples, but an increase in the M–P–C angles and a concomitant decrease in C–P–C angles helps to reduce all three $\theta/2$ values and leads to a cone angle of 176°.

In a relatively uncrowded environment, the $(o\text{-tol})_3\text{P}$ ligand in $[(o\text{-tol})_3\text{PHgCl}\cdot\text{ClO}_4]_2$[12] adopts a propeller conformation (Figure 3c) with Hg–P–C–C(H) torsion angles close to 128° and a maximum cone angle of 198° close to the value predicted (194°). The ligand profile (Figure 2d) shows clearly that there are large gaps of the same order of magnitude as those found in the Cy_3P system. When the $(o\text{-tol})_3\text{P}$ ligand is subjected to steric stress the propeller conformation is changed considerably to make even bigger gaps between the aromatic rings and to decrease the ligand cone angle (Table I). Figures 2e and 2f show the profiles for $(o\text{-tol})_3\text{P}$ in $[(o\text{-tol})_3\text{PHg(OAc)}_2]_2$[19] and in $((o\text{-tol})_3\text{P})_2\text{PtI}_2$,[20] respectively; the cone angles and torsion angles defining the orientation are given in Table I. That $[(o\text{-tol})_3\text{PHg(OAc)}_2]_2$ occurs as a dimer whereas $t\text{-Bu}_3\text{PHg(OAc)}_2$ is a monomer clearly reveals that although the $(o\text{-tol})_3\text{P}$ ligand has a larger cone angle, the greater gaps between the tolyl rings allow the formation of a dimer which is essentially isostructural with $[\text{Cy}_3\text{PHg(NO}_3)_2]_2$ and $[\text{Cy}_3\text{PHg(OAc)}_2]_2$. In the very overcrowded $((o\text{-tol})_3\text{P})_2\text{PtI}_2$,[20] one of the tolyl rings is rotated until the Pt–P–C–C(H) torsion angle is close to 0°. The $(o\text{-tol})_3\text{P}$ ligand is effectively locked in this conformation by the bulky iodine atoms. Our inability to induce ortho metalation in $((o\text{-tol})_3\text{P})_2\text{PtI}_2$ can thus be explained; the ligand conformation is locked, with no methyl group near the platinum, by the bulky iodine atoms. An essentially identical overcrowded conformation is found for $(o\text{-tol})_3\text{P}$ in $((o\text{-tol})_3\text{P})_2\text{IrClCO}$.[21]

Acknowledgment. National Research Council of Canada Operating Grants (to G.F. and E.C.A.) are gratefully acknowledged.

Registry No. $[\text{Cy}_3\text{PHg(SCN)}_2]_n$, 67124-77-0; $[\text{Cy}_3\text{PHg(NO}_3)_2]_2$, 63181-12-4; $[\text{Cy}_3\text{PHg(OAc)}_2]_2$, 67124-81-6; $(\text{Cy}_3\text{P})_2\text{Hg(OAc)}_2$, 66161-25-9; $(\text{Cy}_3\text{P})_2\text{Hg(ClO}_4)_2$, 67124-82-7; $(\text{Cy}_3\text{P})_3\text{Pt}$, 63175-89-3; $(\text{Cy}_3\text{P})_2\text{PtI}_2$, 50725-85-4; $t\text{-Bu}_3\text{PHg(OAc)}_2$, 66119-71-9; $t\text{-Bu}_3\text{PHg}_2\text{(SCN)}_4$, 67238-54-4; $t\text{-Bu}_3\text{PNiBr}_3^-$, 67124-83-8; $[(o\text{-tol})_3\text{PHgCl}\cdot\text{ClO}_4]_2$, 67124-85-0; $[(o\text{-tol})_3\text{PHg(OAc)}_2]_2$, 67124-86-1; $((o\text{-tol})_3\text{P})_2\text{PtI}_2$, 67124-87-2; $((o\text{-tol})_3\text{P})_2\text{IrClCO}$, 56487-57-1.

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Convenient Multigram Syntheses of Uranium Pentafluoride and Uranium Pentaethoxide

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Received June 28, 1978

The chemistry of uranium in unusual oxidation states and coordination environments continues to be a subject of great interest.[1] One of the least studied valencies is the +V state, at least in part due to misconceptions concerning the stability of U(V) with respect to disproportionation and the difficulty in preparing suitable uranium(V) precursors for compound synthesis. However, it is becoming clear that pentavalent uranium in the proper ligand and solvent environment is a stable, interesting entity for which an extensive chemistry is developing.[2–4]

Perhaps the most useful precursors for U(V) compound synthesis are uranium pentafluoride[4] and uranium pentaethoxide.[5] The standard synthesis of $\text{U(OC}_2\text{H}_5)_5$, from UCl_4 and sodium ethoxide in the presence of an oxidant, is a tedious procedure which frequently gives poor yields.[6] Several syntheses of uranium pentafluoride have been reported, but each suffers from certain disadvantages. For example, the reactions of UF_4 and F_2,[7] or of HF with UCl_5 or UCl_6,[8] yield UF_5 but require facilities for handling the highly corrosive materials F_2 and HF. Other reported procedures require elevated temperatures ($\text{UF}_4 + \text{UF}_6$)[9] of inconvenient starting materials (NOUF_6),[10] produce mixtures (NH_4UF_7 pyrolysis or $\text{UF}_6 + \text{HBr}$),[11,12] yield small quantities of product ($\text{UF}_6 + \text{SOCl}_2$ or photolysis of UF_6),[13,14] or produce impure products.

Recently, we have been investigating pentavalent uranium in a variety of chemical environments[4] and have found UF_5 to have an extensive chemistry in nonaqueous solvents. We report here an easy multigram synthesis of pure $\beta\text{-UF}_5$ by a method which obviates the necessity for metal vacuum lines or high-temperature apparatuses. Also, we report a convenient one-step synthesis of the useful material $\text{U(OC}_2\text{H}_5)_5$ from $\beta\text{-UF}_5$.

Experimental Section

Standard Schlenk, vacuum-line, and inert atmosphere box techniques were used throughout this study for manipulating the air-sensitive samples. Ethanol was dried by distillation from magnesium turnings. Sodium ethoxide was prepared by direct reaction of sodium hydride with dry ethanol, followed by vacuum drying. Uranium hexafluoride was purified by a series of trap-to-trap distillations at −41 °C. Carbon monoxide, 99.9% pure, Matheson Gas Products, was passed through a liquid-nitrogen trap and used without further purification. Uranium was determined gravimetrically as the precipitated uranyl bis(8-hydroxyquinolate), $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2\cdot\text{C}_9\text{H}_7\text{NO}$,