Notes

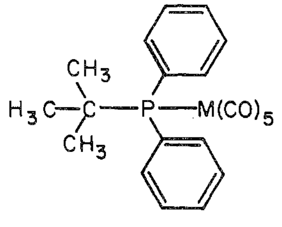
Contribution from the Department of Chemistry,
Worcester Polytechnic Institute, Worcester, Massachusetts 01609

Stereodynamics of *tert*-$C_4H_9(C_6H_5)_2PM(CO)_5$ Complexes ($M = Cr, Mo, W$). Direct Observation of Hindered *tert*-Butyl Rotation Using Hydrogen-1 Dynamic Nuclear Magnetic Resonance Spectroscopy

C. Hackett Bushweller*[1] and Marilyn Z. Lourandos

Received March 13, 1974 AIC40172J

Although some data exist concerning the rate of rotation about the carbon-phosphorus single bond in *tert*-butylphosphines,[2] *tert*-butylphosphine oxides and sulfides,[2a] and *tert*-butylphosphine-boranes,[3] no reports have been forthcoming on the effect of metal complexation on the dynamics of carbon-phosphorus single bond rotation. In light of the fact that phosphines are encountered widely as ligands in metal complexes and the nature of the phosphine ligand may bear significantly on the chemical reactivity of a complex, information regarding the conformational preference and dynamics of symmetric and asymmetric phosphines in metal complexes is required for a complete understanding of chemcial behavior. This report concerns the direct observation of slow *tert*-butyl rotation in complexes **1**-**3** using the ^1H dnmr method and the existence of a significant dependence of $^3J_{PCCH}$ on stereochemistry.



1, M = Cr
2, M = Mo
3, M = W

Examination of the ^1H dnmr spectrum of **3** (6% wt/v in $CHClF_2$) at −42° revealed a symmetrical doublet resonance (δ 1.34; average $^3J_{PCCH} = 15.0$ Hz) consistent with rapid *tert*-butyl rotation on the dnmr time scale.[2a,3] At lower temperatures (Figure 1), the *tert*-butyl doublet resonance broadens asymmetrically consistent with slowing a rate process on the dnmr time scale and sharpens into the spectrum observed at −128.7° (Figure 1). A complete dnmr line shape analysis using computer program DNMR3[4] at −128.7° is consistent with a spectrum composed of a large doublet resonance (6 H; δ 1.36; $^3J_{PCCH} = 17.5$ Hz) and a smaller doublet (3 H; δ 1.28; $^3J_{PCCH} = 10.0$ Hz) consistent with *slow tert-butyl rotation* on the dnmr time scale (eq 1). The smaller doublet (3 H) is assigned to the methyl trans to W-$(CO)_5$ and the larger doublet (6 H) to the two methyls gauche to $W(CO)_5$. A complete dnmr line shape analysis in the regions of intermediate and fast rates of *tert*-butyl rotation required the use of $^3J_{PCCH}$ values of the *same* relative signs and gave the activation parameters for *tert*-butyl rotation compiled in Table I. The large errors in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ result from short T_2 values (*i.e.*, broad lines) observed at low temperatures and the difficulties associated with selecting T_2 values in the region of exchange broadening. The methods of selecting effective T_2 values and assigning error limits to $\Delta H^\ddagger$ and $\Delta S^\ddagger$ have been discussed in detail in previous papers.[5] The errors assigned to $^3J_{PCCH}$ in Table I were determined by obtaining first an essentially perfect fit of theoretical to experimental dnmr spectra and then varying $^3J_{PCCH}$ until a clearly poor fit was evident.

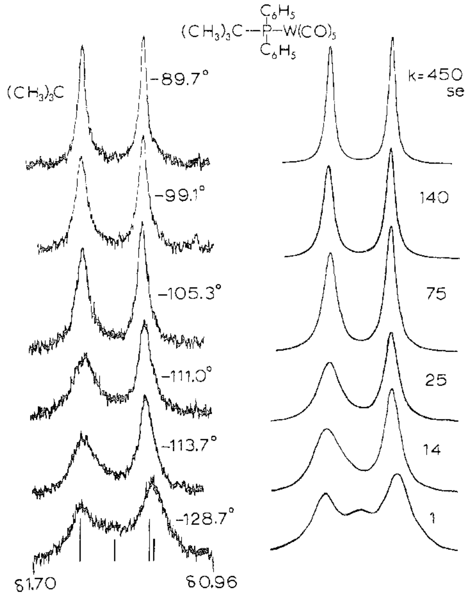
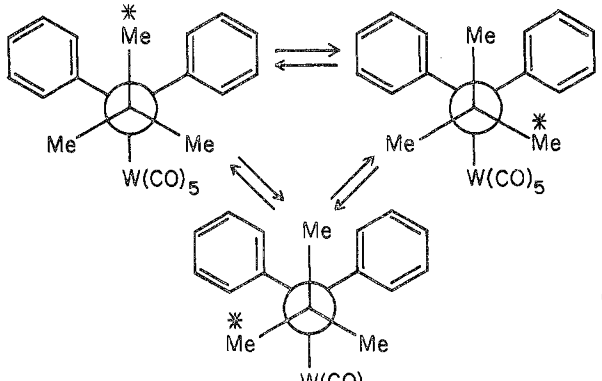


Figure 1. The ^1H dnmr spectra of the *tert*-butyl group of *tert*-C_4H_9-$(C_6H_5)_2PW(CO)_5$ in $CHClF_2$ and theoretical spectra calculated as a function of the rate of *tert*-butyl rotation (*k* is the first-order rate constant for disappearance of a methyl group from any one of the three sites on the *tert*-butyl group).



(1)

---

[1] Alfred P. Sloan Research Fellow, 1971-1974; Camille and Henry Dreyfus Teacher-Scholar, 1972-present.

[2] (a) C. H. Bushweller and J. A. Brunelle, *J. Amer. Chem. Soc.*, 95, 5949 (1973); C. H. Bushweller, J. A. Brunelle, W. G. Anderson, and H. S. Bilofsky, *Tetrahedron Lett.*, 3261 (1972); (b) J. B. Robert and J. D. Roberts, *J. Amer. Chem. Soc.*, 94, 4902 (1972).

[3] C. H. Bushweller and J. A. Brunelle, *Tetrahedron Lett.*, 893 (1974).

[4] D. A. Kleier and G. Binsch, *J. Magn. Resonance*, 3, 146 (1970).

[5] G. Binsch, *Top. Stereochem.*, 3, 97 (1968); K.-I. Dahlquist and S. Forsen, *Acta Chem. Scand.*, 24, 694 (1970); C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *Tetrahedron*, 27, 5761 (1971); C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *ibid.*, 28, 2697 (1972).

Table I. Activation and Dnmr Parameters for *tert*-Butyl Rotation in *tert*-$C_4H_9(C_6H_5)_2PM(CO)_5$ Complexes

Compd	Slow-exchange *tert*-butyl dnmr parameters		$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, gibbs	$\Delta G^{\ddagger}$, kcal/mol (temp, °C)
	δ,[a] ppm	$^3J_{PCCH}$, Hz			
tert-$C_4H_9(C_6H_5)_2PCr(CO)_5$	1.36 (6 H)	16.5 ± 0.5			8.4 ± 0.2 (−109.8)
	1.22 (3 H)	10.0 ± 0.5			
tert-$C_4H_9(C_6H_5)_2PMo(CO)_5$	1.33 (6 H)	17.8 ± 0.5			8.3 ± 0.2 (−110.0)
	1.25 (3 H)	10.2 ± 0.5			
tert-$C_4H_9(C_6H_5)_2PW(CO)_5$	1.36 (6 H)	17.5 ± 0.5	8.7 ± 0.6	2 ± 6	8.3 ± 0.2 (−113.7)
	1.28 (3 H)	10.0 ± 0.5			

[a] Downfield from tetramethylsilane.

Table II. Activation Parameters for *tert*-Butyl Rotation in Selected *tert*-Butylphosphines

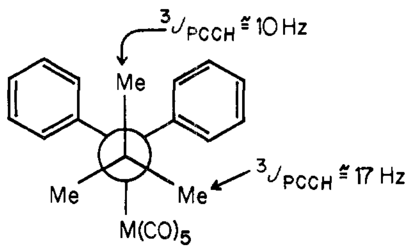
Compd	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, gibbs	$\Delta G^{\ddagger}$, kcal/mol (temp, °C)
(*tert*-$C_4H_9)_3P$	9.0 ± 0.4[a]	2 ± 4	8.6 ± 0.1 (−103)
(*tert*-$C_4H_9)_3PS$	9.5 ± 0.4[a]	−5 ± 4	10.5 ± 0.1 (−72)
(*tert*-$C_4H_9)_3PBH_3$	10.0 ± 0.2[b]	−2 ± 2	10.4 ± 0.1 (−68)
(*tert*-$C_4H_9)_2ClPBH_3$	7.0 ± 0.4[b]	0 ± 5	6.8 ± 0.1 (−141)
tert-$C_4H_9(C_6H_5)_2PW(CO)_5$	8.7 ± 0.6[c]	2 ± 6	8.3 ± 0.2 (−114)
tert-$C_4H_9(CH_3)_2NBH_3$	11.2 ± 0.3[d]	6 ± 2	10.0 ± 0.1 (−79)

[a] See ref 2a. [b] See ref 3. [c] This work. [d] C. H. Bushweller, W. J. Dewkett, J. W. O'Neil, and H. Beall, *J. Org. Chem.*, **36**, 3782 (1971).

Very similar changes were observed for the chromium (**1**) and molybdenum (**2**) analogs of **3**. Slow-exchange *tert*-butyl chemical shifts and free energies of activation ($\Delta G^{\ddagger}$) for *tert*-butyl rotation are listed in Table I.

In light of other available data concerning rotation about the C-P bond in various *tert*-butylphosphines,[2,3] a comparison of the free energies of activation ($\Delta G^{\ddagger}$) for *tert*-butyl rotation in **1-3** (Table I) reveals a remarkable insensitivity to variation of the metal pentacarbonyl moiety. However, in light of X-ray crystallographic data for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ revealing very similar metal covalent radii [Cr(1.48 ± 0.01 Å), Mo (1.62 ± 0.01 Å)][6] and metal-carbon bond lengths [Cr-C (1.92 ± 0.04 Å), Mo-C (2.08 ± 0.04 Å), W-C (2.06 ± 0.04 Å)][7] and similar Cr-P [2.422 Å in $(C_6H_5)_3PCr(CO)_5$][8] and Mo-P bond lengths [2.517 Å in $(C_6H_5)_2C_6H_4CH{=}CHCH_3PMo(CO)_4$],[9] it is not surprising that the three metal pentacarbonyl groups have the same effective steric size in the context of hindering *tert*-butyl rotation.

Obtaining ^1H dnmr spectra for **1-3** under conditions of slow *tert*-butyl rotation (*e.g.*, Figure 1, −128.7°) also unveiled a significant dependence of $^3J_{PCCH}$ on molecular geometry. $^3J_{PCCH}$ for the methyl group trans to the metal in **1-3** (~10 Hz) is significantly smaller than that for the two methyls gauche to the metal (~17 Hz), *e.g.*, **4**. This



4

situation is similar to that in uncomplexed *tert*-butylphosphines[2] and *tert*-butylphosphine-boranes[3] and may prove to be a useful probe into free phosphine and complexed phosphine stereochemistry.

Only a limited amount of data is available concerning the dynamics of carbon-phosphorus single-bond rotation and only a qualitative picture of the effective hindering potential associated with a given substituent may be deduced. Indeed, a direct comparison between the free *tert*-butyldiphenylphosphine and complexes **1-3** is not possible because no *tert*-butyl dnmr peak separation was observed in the free phosphine.[2a] However, for purposes of comparison, activation parameters for *tert*-butyl rotation in selected free and complexed *tert*-butylphosphines as well as an amine-borane are compiled in Table II.

Experimental Section

The ^1H dnmr spectra were obtained using a Varian HR-60A spectrometer equipped with a custom-built variable-temperature probe.[10]

Complexes **1-3** were prepared according to the procedure of Grim and coworkers.[11]

Acknowledgment. We are grateful to the National Science Foundation (Grant No. GP-18197) for support.

Registry No. **1**, 18497-57-9; **2**, 18534-32-2; **3**, 18534-40-2.

(6) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, **5**, 1851 (1966).

(7) L. O. Brockway, R. V. G. Ewens, and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

(8) H. J. Plastos, J. M. Stewart, and S. O. Grim, *J. Amer. Chem. Soc.*, **91**, 4326 (1969).

(9) H. Luth, M. R. Truter, and A. Robson, *J. Chem. Soc. A*, 28 (1969).

(10) F. R. Jensen, L. A. Smith, C. H. Bushweller, and B. H. Beck, *Rev. Sci. Instrum.*, **43**, 894 (1972).

(11) S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, **89**, 5573 (1967).

Contribution from the Francis Bitter National Magnet
Laboratory, Massachusetts Institute of Technology, Cambridge,
Massachusetts 02139, and from the Departments of Chemistry,
Northeastern University, Boston, Massachusetts 02115, and
University of North Carolina, Chapel Hill, North Carolina 27514

Magnetic Field Mossbauer Spectroscopy of Metal Cluster Systems. $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$

R. B. Frankel,* W. M. Reiff, T. J. Meyer, and J. L. Cramer

Received March 19, 1974 AIC40188+

We report the use of Mossbauer spectroscopy in external magnetic fields to study certain features of the electronic structure of the tetrahedral metal-metal bonded clusters $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ (Figure 1). Specifically, we are interested in ascertaining whether the unpaired electron in the paramagnetic monocation is localized on the iron sites or is extensively delocalized to the ligands. The question is relevent because in certain iron-sulfur proteins, the electrons involved in the oxidation and re-

---

* To whom correspondence should be addressed at the Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology.