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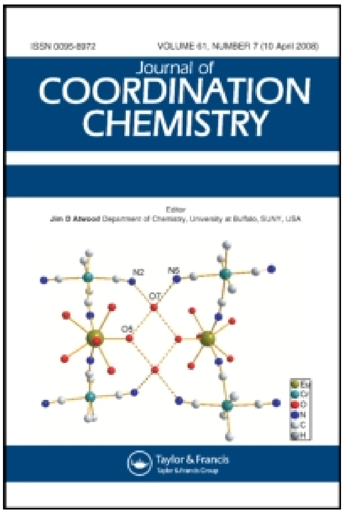

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A RE(I) COMPLEX OF THE PHOSPHINE OBTAINED BY REACTING DIPHENYLPHOSPHINE WITH *TERT*-BUTYL ACRYLATE: A PHOSPHINE-ESTER COMPLEX THAT CAN BE CONVERTED TO THE PHOSPHINE-ACID COMPLEX UNDER MILD CONDITIONS

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A RE(I) COMPLEX OF THE PHOSPHINE OBTAINED BY REACTING DIPHENYLPHOSPHINE WITH *TERT*-BUTYL ACRYLATE: A PHOSPHINE-ESTER COMPLEX THAT CAN BE CONVERTED TO THE PHOSPHINE-ACID COMPLEX UNDER MILD CONDITIONS

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The base-catalyzed reaction between diphenylphosphine and *tert*-butyl acrylate results in the formation of $Ph_2PCH_2CH_2CO_2C(CH_3)_3$ (**I**). This ligand readily forms a Re(I) complex of the type *fac*-$Re(CO)_3Cl$ $(\mathbf{I})_2$ that can be converted to the corresponding $Ph_2PCH_2CH_2CO_2H$ complex under mild conditions by using hydrogen chloride in dioxane. Refluxing this carboxylic-acid-containing complex in acidified methanol provides the methyl ester analog of **I**. In contrast, this methyl ester-containing complex is stable to the ester cleavage reaction conditions used for **I**. Molecular mechanics calculations on **I** and the related methyl ester ligand provide data that are consistent with the conclusion that these phosphine-esters have cone angles that are *ca.* 10° smaller than that of Ph_3P.

KEYWORDS: rhenium(I), phosphine ester, phosphine acid

INTRODUCTION

Ligands that can enhance the water solubility of inorganic and organometallic complexes are the focus of considerable recent attention. For example, there has been considerable interest in phosphines functionalized with groups including $-OH$[1a], $-P(O)(OR)_2$[1a], or, in particular, $-SO_3^-$[1b,c]. Carboxylic acid functionalized ligands have also been studied for this purpose. $(\eta^5\text{-}C_5H_4CO_2H)_2W_2(CO)_6$ is water soluble as is the phosphine-acid ligand shown in Figure 1[1e]. Our recent interest in phosphine-ester hybrid ligands prepared from acrylates[2] has prompted us to investigate the potential for these to be precursors for phosphine-carboxylic acid ligands. Further, we note that ester groups could, for example, serve to protect acid groups until the P(III) centers were coordinated in a predetermined fashion, and in our hands, both the phosphine-ester ligands and their complexes have proved to be easy to prepare and purify, also an advantage. Finally, that phosphine-esters have

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proved to be versatile ligands in their own right[3] provided an additional impetus for the study.

In accord, we have elected to undertake the preparation and study of $Ph_2PCH_2CH_2CO_2C(CH_3)_3$ (**I**), a ligand based on *tert*-butyl acrylate. This system was selected because *tert*-butyl esters are stable under mildly basic conditions, but they readily cleave under acidic conditions.[4] For the latter, trifluoroacetic acid in dichloromethane or hydrogen chloride in ether at temperatures as low as 0°C have been used. This is in contrast to the conditions required to hydrolyze other esters such as $PhCH_2CO_2CH_3$ for which a typical set of conditions involves the use of LiI in refluxing pyridine.[4d,5]

It is also noted that nitrile groups in the related ligands, $Ph_{3-x}P(CH_2CH_2CN)_x$, and their complexes have been hydrolyzed to the corresponding carboxylic acids. Aqueous alkaline hydrolysis of $Ph_2PCH_2CH_2CN$ has been reported to provide the corresponding acid,[6] and aqueous sulfuric acid at 120 °C has been used to hydrolyze the CN groups in $Au[P(CH_2CH_2CN)_3]_2Cl$.[7]

Herein we report the syntheses of **I**, $Re(CO)_3Cl(I)_2$ (**II**), $Re(CO)_3Cl(Ph_2PCH_2CH_2CO_2H)_2$ (**III**), and $Re(CO)_3Cl(Ph_2PCH_2CH_2CO_2CH_3)_2$ (**IV**). Also reported are selected spectroscopic data for **I**–**IV** and proposed structural properties for **I** from computational methods.

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EXPERIMENTAL

Materials, Instruments and Methods

Ph_2PH, $H_2CC(H)CO_2C(CH_3)_3$, and HCl in dioxane (4.0 M) were obtained from Aldrich Chemical Co., Inc. $Re_2(CO)_{10}$ was purchased from Strem Chemicals, Inc., and converted to $Re(CO)_5Cl$ by a reported procedure.[8] Other materials were obtained from the departmental stores. Reactions were carried out under a blanket of argon.

NMR and IR spectra were obtained by using a Varian Gemini 200 instrument and either a Perkin Elmer 1760-X or a Nicolet 5ZDX spectrophotometer, respectively. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN, or the Micro Lab in the Department of Chemistry, University of Illinois, Urbana IL. Analytical data are presented in Table 1.

The energy minimized structures used to generate Figure 2 and data for the torsion and cone angle measurements were obtained using the default parameters

Table 1 Analytical data

Compound	*Analyses*	(Found)	(Calcd) %)
	C	H	Cl
I	72.50	7.36	--
	(72.59)	(7.37)	
II	52.60	4.98	3.72
	(52.70)	(4.96)	(3.79)
III·1/8 CH_2Cl_2	47.41	3.84	5.82
	(47.77)	(3.66)	(5.32)
IV·1/8 CH_2Cl_2	49.06	4.02	4.91
	(49.01)	(4.01)	(5.15)

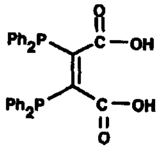

Figure 1. Phosphine based on maleic acid

resident in PCMODEL version 5, Serena Software. The SYBYL program set, TRIPOS Associates, was used to measure the torsion and cone angles.

Syntheses and Reactions

$Ph_2PCH_2CH_2CO_2C(CH_3)_3$ (I)

Ph_2PH (5.35 g, 28.7 mmol) and $H_2CCHCO_2C(CH_3)_3$ (12.14 g, 95.5 mmol) and 2 drops of tetraethyl ammonium hydroxide were added to 50 mL of deoxygenated acetonitrile. The mixture was warmed to 60°C for 4 h, cooled to ambient temperature, and the solvent was removed to provide a tan-colored solid. This solid was recrystallized from 20 mL of ethanol to provide 6.04 g (66.9%) of product.

$Re(CO)_3Cl(I)_2$ (II)

$Re(CO)_5Cl$(0.52 g, 1.44 mmol) and **I** (1.13 g, 3.59 mmol) were refluxed in 75 mL of benzene for 4 h. The solvent was evaporated and the resulting solid recrystallized from a mixture of dichloromethane, 2-propanol and heptane to provide 1.26 g (94.0%) of product.

$Re(CO)_3Cl(Ph_2PCH_2CH_2CO_2H)_2$ (III)

II (0.50 g, 0.54 mmol) and 15 mL of HCl in dioxane (4.0 M) were heated to 65°C for 12.5 h. The solvent mixture was removed by using a rotary evaporator, and the resulting solid was washed with 5 mL of dichloromethane providing 0.42 g (93.3%) of **III**.

$Re(CO)_3Cl(Ph_2PCH_2CH_2CO_2CH_3)_2$ (IV)

III (0.50 g, 0.61 mmol) was dissolved in 15 mL of warm methyl alcohol that contained 1 drop of HCl in dioxane (4.0 M). The mixture was refluxed in a 50 mL Erlenmeyer flask for 1 h. Methyl alcohol was added periodically to maintain the solvent level. Colorless solid began to be evident upon onset of boiling. The colorless solid was collected on a filter and recrystallized from a mixture of dichloromethane, heptane and 2-propanol to provide 0.26 g (50.0%) of **IV**.

Reaction of IV with HCl in dioxane

IV (0.21 g, 0.25 mmol) was dissolved in 3 mL of dichloromethane, treated with 6 mL of HCl in dioxane (4.0 M) and refluxed for 12.5 h. The resulting solution was evaporated to dryness, providing a yellow residue. The residue was washed with

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2 x 5 mL of methanol, and the remaining solid was recrystallized from a mixture of dichloromethane, 2-propanol and heptane to provide 0.19 g of crystals with properties that matched those of **IV**.

RESULTS AND DISCUSSION

*Synthesis of **I** and Computation-Based Studies of Phosphine-Ester Ligands*

The reaction between Ph_2PH an $H_2CCHCO_2C(CH_3)_3$ proceeds under mild conditions to produce good yields of $Ph_2PCH_2CH_2CO_2C(CH_3)_3$ (**I**). Analytically pure samples of **I** can readily be obtained by fractional distillation (bp *ca.* 190°C at 0.5 mmHg) or crystallization from ethanol. In contrast to the phosphines obtained from $H_2CCHCO_2CH_3$ and $H_2CC(CH_3)HCO_2CH_2CH_3$ which are oils at ambient conditions;[2] **I** readily forms crystals, and these can be handled in air with a minimum of oxidation. As summarized in Table 2, the spectroscopic properties of **I** are entirely consistent with the formulations and connectivities proposed. The ^1H NMR spectrum is dominated by a sharp singlet at δ 1.45 that is assigned to the CH_3 group protons, and the ^{13}C NMR spectrum shows the expected P-C couplings.

In order to help assess the properties of this ligand, energy minimized structures of **I**, the corresponding methyl ester, and Ph_3P have been obtained by using the default parameters associated with the PCMODEL program set, and these data have been evaluated by using the SYBYL program set. For a broader comparison, the latter program has also been used to evaluate the previously reported[9] X-Ray data for Ph_3P. A particular goal was to obtain information regarding the possible steric impact of the remotely-located *tert*-butyl group on the phosphorus(III) center. To help quantify the difference and similarities for the two ester ligands, the torsion angles for these phosphines were determined by the method described by Dunitz.[10] Basically, this method involves measuring the torsion angles from the ortho-positioned carbons through the ipso carbon and phosphorus atoms to a centroid defined by the three ipso carbons. With this convention, larger positive values correspond to a greater clockwise rotation around the P-C bond. The data, presented in Table 3, indicate that both the *tert*-butyl and methyl ester ligands have one phenyl ring that is nearly vertical with respect to the P-C bond. However, for

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Table 2 Selected spectroscopic data

Compound	NMR[a]						IR			
		1H	13c							
	31P	CH_3	PCH_2	CH_2	C(O)	OCR	ν(C=O)	ν(C≡O)		
I	-17.1	1.45	23.1 (11.7)	32.0 (19.0)	172.5 (15.2)	80.6 (s)	1730	—		
II	- 4.6	1.40 (s)	21.1 (s)	30.2 (m)	171.5 (s)	80.9	1720	2030	1955	1910
III[b]	- 5.7	—	—	—	—	—	1710	2030	1950	1920
IV	- 4.9	3.60 (s)	20.8 (s)	28.9 (m)	172.7 (s)	51.9	1735	2028	1945	1908

[a] H_3PO_4 and TMS standards; chemical shifts in ppm, coupling constants, J(PC), in Hz; coupling constants for the doublets are presented in parentheses; s = singlet, m = multiplet; recorded in $CDCl_3$. [b] Not sufficiently soluble for standard C-13 methods.

Table 3 Torsion angles for I and the corresponding methyl ester

	Torsion Angles, Degrees[a]	
Phosphine-ester	Ph(1)	Ph(2)
tert-butyl	3.8 (−175.8)	36 (−143.5)
methyl	172.7(−6.4)	124.8 (−55.6)

[a] Values for both ortho carbons are listed, PCMODEL data set.

the former ligand, the second phenyl is more nearly vertical than in the latter. From another perspective, the two phenyl rings in the former and latter are rotated a total of 40° and 62°, respectively, from vertical positions. Tolman cone angles[12] have also been determined from these three energy-minimized and single X-ray data sets. The cone angle values (from $\theta/2$ measurements) are 145° and 143°, respectively, for the *tert*-butyl and methyl ester ligands, and 153° for triphenylphosphine. Even though the contributions from the more vertical phenyl rings are greater for the *tert*-butyl ligand (112° *vs.* 104°) the difference is nearly offset by the fact that the former ligand has a $\theta/2$ value for the alkyl group that is 10° smaller. For triphenyl phosphine, the computation-based and X-Ray data sets gave rise to cone angles of 153° and 159°, respectively. These values compare to the values of 145°[11a] and 157°[11b] for triphenylphosphine obtained from CPK models and an MM2-based data set, respectively. Given these data, it is concluded that both of the phosphine-ester ligands have cone angles that are *ca.* 10° smaller than triphenylphosphine, a difference that is consistent with previously reported studies of alkyl phosphines of the type Ph_2PR.[11] Further, it is also concluded that the *tert*-butyl group has a minimal impact on the molecular geometry near the phosphorus(III) lone pair. A representation of the energy minimized structure of I is shown in Figure 2.

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Re-Containing Complexes and Cleavage of the Ester Group

I reacts with $Re(CO)_5Cl$ to provide a complex of the type $Re(CO)_3Cl(I)_2$. The complex is easy to purify because it is stable, and it also readily forms crystals that are analytically pure. The $\nu(CO)$ pattern is consistent with the usual *fac* isomer (see Figure 3) substitution pattern.[12]

Cleavage of the tertiary carbon-to-oxygen bonds has been accomplished at 65°C with 4.0 M HCl in dioxane. The resulting carboxylic-acid-containing complex is sparingly soluble in dichloromethane and chloroform but readily soluble in polar

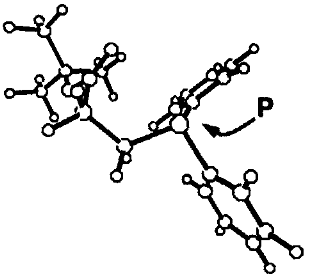

Figure 2. Structure of I obtained *via* computational methods.

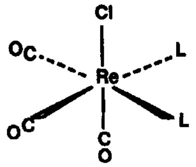

Figure 3. Proposed coordination geometry for the Re complexes (L = **I**).

solvents including acetone and DMSO. The cleavage reaction was also attempted at both 20° and 10°C, but the reaction was observed to be slow under these conditions. As for **II**, the infrared spectrum of **III** is also dominated by 3 very strong ν(CO) (Re-CO) bands. In addition however, there is a ν(CO) (C-CO) band at 1710, and a series of small bands between *ca.* 3000 and 2600 cm^{-1}. These data are consistent with the presence of a *fac* isomer in which the carboxylic acid groups are hydrogen bonded.

Complex **III** is readily esterified to the corresponding methyl ester complex, **IV**. Refluxing **III** in methanol that contains a drop of 4.0 M hydrogen chloride in dioxane immediately gives rise to a noticeable precipitate that corresponds to **IV**. We have not attempted to maximize the yield of **IV**, and, as such a yield of 50% has been obtained. This complex, **IV**, has spectral properties (see Table 2), that indicate it is similar in structure complexes to **II** and **III**. As expected, a major difference in the ^1H spectra is the presence of a singlet at δ 3.60 that corresponds to the CH_3 group. Treating **IV** with hydrogen chloride in dioxane under conditions that cleaved the ester group in **II** provided a product that had properties which were identical to the starting material. Neither spectroscopic (NMR and IR) measurements nor mass balance data suggested that a significant degree of ester cleavage had taken place. These observations are consistent with the conclusion that the ester cleavage reaction observed for **II** likely proceeds by the usual mechanism[4d] and not by, for example, an unselective metal-mediated process.

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Acknowledgments

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References

1. (a) A.M. Herring, B.D. Steffey, A. Miedaner, S.A. Wander and D.L. DuBois, *Inorg. Chem.*, **34**, 1100 (1995). (b) H. Ding, B.E. Hanson, T. Bartik and B. Bartik, *Organometallics*, **13**, 3761 (1994). (c) T. Bartik, B.B. Bunn, B. Bartik and B.E. Hanson, *Inorg. Chem.*, **33**, 164 (1994). (d) T. Bartik, B. Bartik, B.E. Hanson, T. Glass and W. Bebout, *Inorg. Chem.*, **31**, 2667 (1992), (e) A. Avey, D.M. Schut, T.J.R. Weakley and D.R. Tyler, *Inorg. Chem.*, **32**, 233 (1993).
2. D.A. Blinn, R.S. Button, V. Farazi, M.K. Neeb, C.L. Tapley, T.E. Trehearne, S.D. West, T.L. Kruger and B.N. Storhoff, *J. Organometal. Chem.*, **393**, 143 (1990).

3 (a) P. Steinert and H. Werner, *Organometallics*, **13**, 2677 (1994). (b) H. Werner, A. Stark, M. Schulz and J. Wolf, *Organometallics*, **11**, 1126 (1992).

4. (a) T.W. Greene and P.G.M. Wuts, *Protective Groups in Organic Synthesis*, (John Wiley and Sons, Inc., New York, 1991), p. 245. (b) R.C Larock, *Comprehensive Organic Transformations*, (VCH Publishers, Inc., New York, 1989), p. 981. (c) J.C. Sheehan and K.R. Henery-Logan, *J. Am. Chem. Soc.*, **81**, 3089 (1959). (d) The Ingold classification system for ester hydrolysis mechanisms has been summarized by March (J. March, Advanced Organic Chemistry (John Wiley and Sons, Inc., New York, 1992) pp. 378–383). Unlike most esters in acidic media where the AAcl mechanism prevails, *tert*-alkyl esters are converted by cleavage of the alkyl group-to-oxygen bond (AAL1 mechanism) with formation of the *tert*-alkyl carbo cation.

5. J. McMurry, *Organic Reactions*, Vol. **24**, W.G. Dauben, ed. (John Wiley and Sons, Inc., New York, 1976), pp. 187–224.

6. (a) R.C. Hinton, F.G. Mann and D. Todd, *J. Chem. Soc*, 5454 (1961). (b) E.P. Kyba and S.T. Liu, *Inorg. Chem.*, **24**, 1613 (1985).

7. Md. N.I. Khan, C. King, J.P. Fackler, Jr., and R.E. Winpenny, *Inorg. Chem.*, **32**, 2502 (1993).

8. R.J. Angelici and A.E. Kruse, *J. Organometal. Chem.*, **22**, 461 (1970).

9. J.J. Daly, *J. Chem. Soc.*, 3799 (1964).

10. E. Bye, W.B. Schweizer and J.D. Dunitz, *J. Am. Chem. Soc.*, **104**, 5893 (1982).

11. (a) C.A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970), (b) M. Chin, G.L. Durst, S.R. Head, P.L. Bock and J.A. Mosbo, *J. Organometal. Chem.*, **470**, 73 (1994). (c) T.L. Brown and K.J. Lee, *Coord. Chem. Rev.*, **128**, 89 (1993). (d) D. White and N.J. Coville, *Adv. Organomet. Chem.*, **36**, 95 (1994).

12. R.J. Angelici, F. Basolo and A.J. Poe, *J. Am. Chem. Soc.*, **85**, 2215 (1963).

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