*Organometallics* **1985**, *4*, 867-871

# A Crystallographic Determination of the Influence of the Trans Ligand on the Bonding of Triphenylphosphine. Crystal and Molecular Structures of Cr(CO)$_4$(PPh$_3$)L (L = PBu$_3$, P(OMe)$_3$, and P(OPh)$_3$)

Michael J. Wovkulich,[1] Jerry L. Atwood,*[2] L. Canada,[2] and Jim D. Atwood*[3]

*Departments of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, and University of Alabama, University, Alabama 35486*

*Received May 2, 1984*

The crystal structures of three complexes *trans*-Cr(CO)$_4$LPPh$_3$ (L = PBu$_3$, P(OMe)$_3$, and P(OPh)$_3$) have been determined to define the influence of the trans ligand on the bonding of PPh$_3$. The Cr–PPh$_3$ bond varies significantly with the trans ligand (L = PBu$_3$, Cr–PPh$_3$ = 2.349 (4) Å; L = P(OMe)$_3$, Cr–PPh$_3$ = 2.364 (6) Å; L = P(OPh)$_3$, Cr–PPh$_3$ = 2.395 (2) Å), shorter for a stronger donor in the trans position. This trans influence suggests a significant component of $\pi$-bonding in the Cr–PPh$_3$ bond. The trans influence does not correlate with the kinetic trans effect for these complexes, indicating transition state effects dominate the reactivity. Chromium–phosphite and –phosphine bond lengths are compared.

## Introduction

The influence that ligands coordinated to a transition metal have on bonding, structures, and spectroscopic properties of the metal center or on other ligands has been a major area of investigation. The influence when ligands have both $\sigma$- and $\pi$-bonding capabilities is often difficult to interpret. Derivatives of hexacarbonylchromium have been extensively investigated with studies of CO stretching frequencies,[4] M–CO bond lengths,[5] $^{31}$P NMR chemical shifts,[6] $^{13}$C NMR chemical shifts,[7] and X-ray crystallography[8-12] to evaluate the binding of CO, phosphites, and phosphines to the chromium. Structural studies of Cr(CO)$_5$P(OPh)$_3$[5] and *trans*-Cr(CO)$_4$(P(OPh)$_3$)$_2$[12] showed a dramatic shortening of the Cr–P bond for the bis-substituted complex. A slight shortening of the Cr–P bond was noted with extent of substitution in *cis*-Cr(CO)$_4$(PH$_3$)$_2$, *fac*-Cr(CO)$_3$(PH$_3$)$_3$, and *cis*-Cr(CO)$_2$(PH$_3$)$_4$.[9-11]

In order to evaluate the effect of the trans ligand on bonding properties of PPh$_3$, we have studied the crystal and molecular structures of Cr(CO)$_4$(PPh$_3$)L [L = PBu$_3$ (Bu = *n*-butyl), P(OMe)$_3$, and P(OPh)$_3$]. These compounds are prepared by reaction of [Cr(CO)$_4$LCl]$^-$ with PPh$_3$ (eq 1).[13,14] The ligands L span a considerable range

$$\mathrm{Cr(CO)_4LCl^- + PPh_3 \rightarrow \mathit{trans}\text{-}Cr(CO)_4PPh_3L + Cl^-} \quad (1)$$

in their bonding capabilities with PBu$_3$ a strong $\sigma$ donor, P(OMe)$_3$ a strong $\sigma$ donor and $\pi$ acceptor, and P(OPh)$_3$ a strong $\pi$-acceptor. The structure of Cr(CO)$_5$PPh$_3$ is known, allowing CO to also be evaluated for a possible trans influence. This set of compounds has added significance since the rates of PPh$_3$ dissociation are known, and the comparison of the *trans influence* and the *trans effect* of octahedral chromium carbonyl complexes can be made.[15-18]

## Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk techniques or an inert-atmosphere glovebox. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer using 1.0-mm NaCl solution cells.

**Materials.** Tetrahydrofuran was refluxed over sodium/benzophenone until dry then distilled under nitrogen prior to use. Methylene chloride was stirred over KOH and then distilled from P$_2$O$_5$. Ethanol was degassed by using freeze–pump–thaw cycles and stored over molecular sieves. Diglyme was purchased from Aldrich Chemical Co. and used as obtained. Et$_4$NCl·H$_2$O was obtained from Aldrich Chemical Co., and Cr(CO)$_6$, PBu$_3$, P(OMe)$_3$, P(OPh)$_3$, and PPh$_3$ were obtained from Strem Chemicals, Inc.

**Preparation of Et$_4$N[Cr(CO)$_5$Cl].** This complex was prepared by a modified version of Abel et al.[19] A mixture of 4.0 g of Cr(CO)$_6$ (1.8 × 10$^{-2}$ mol) and 3.4 g of Et$_4$NCl·H$_2$O (1.8 × 10$^{-2}$ mol) in diglyme/THF (20 mL/20 mL) was refluxed under argon for 4 h giving an orange solution. The presence of THF is necessary to eliminate the problem of sublimation of unreacted Cr(CO)$_6$ and also minimizes decomposition of the product. After the mixture was allowed to cool to room temperature, removal of THF via vacuum followed by addition of 100 mL of pentane caused precipitation of the product Et$_4$N[Cr(CO)$_5$Cl]. This yellow solid was washed with pentane and then dried in vacuo overnight.

**Preparation of Et$_4$N[LCr(CO)$_4$Cl] (L = PBu$_3$, P(OMe)$_3$, and P(OPh)$_3$).** These complexes were prepared by applying an adaptation of the procedure of Schenk.[13,14] To a THF solution (20 mL) of 1.0 g of Et$_4$N[Cr(CO)$_5$Cl] (2.8 × 10$^{-3}$ mol) was added an excess of the ligand L, and the mixture was allowed to react at room temperature under argon for a specified time. The amounts of L used and reaction times are as follows: 2 mL of PBu$_3$ (8.0 × 10$^{-3}$ mol), 10 min; 1 mL of P(OMe)$_3$ (8.5 × 10$^3$ mol), 30 min; 2 mL of P(OPh)$_3$ (7.6 × 10$^{-3}$ mol), 1$^1/_2$ h. For L = PBu$_3$ and P(OMe)$_3$, the reactions were accompanied by noticeable

---

(1) State University of New York at Buffalo.

(2) University of Alabama.

(3) State University of New York at Buffalo. Alfred P. Sloan Foundation Fellow.

(4) Wovkulich, M. J.; Atwood, J. D. *J. Organomet. Chem.* **1979**, *184*, 77.

(5) Plastas, H. J.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* **1973**, *12*, 265.

(6) Grim, S. O.; Wheatland, D. A.; McFarlane, W. *J. Am. Chem. Soc.* **1967**, *89*, 5573.

(7) Bodner, G. M. *Inorg. Chem.* **1975**, *14*, 2694.

(8) Holladay, A.; Churchill, M. R.; Wong, A.; Atwood, J. D. *Inorg. Chem.* **1980**, *19*, 2195.

(9) Huttner, G.; Schelle, S. *J. Organomet. Chem.* **1969**, *19*, P9.

(10) Huttner, G.; Schelle, S. *J. Cryst. Mol. Struct.* **1971**, *1*, 69.

(11) Guggenberger, L. J.; Klabunde, U.; Schunn, R. A. *Inorg. Chem.* **1973**, *12*, 1143.

(12) Preston, H. S.; Stewart, J. M.; Plastas, H. J.; Grim, S. O. *Inorg. Chem.* **1972**, *11*, 161.

(13) Schenk, W. A. *J. Organomet. Chem.* **1979**, *179*, 253.

(14) Schenk, W. A. *J. Organomet. Chem.* **1980**, *184*, 195.

(15) Wovkulich, M. J.; Atwood, J. D. *Inorg. Chem.* **1980**, *19*, 2608.

(16) Wovkulich, M. J.; Atwood, J. D. *Organometallics* **1982**, *1*, 1316.

(17) Wovkulich, M. J.; Atwood, J. D. *J. Organomet. Chem.* **1980**, *184*, 77.

(18) Atwood, J. D.; Wovkulich, M. J.; Sonnenberger, D. C. *Acc. Chem. Res.* **1983**, *16*, 350.

(19) Abel, E. W.; Butler, S. S.; Reid, J. O. *J. Chem. Soc.* **1963**, *2068*.

0276-7333/85/2304-0867$01.50/0

**Table I. Crystallographic Parameters for the Compounds *trans*-$Cr(CO)_4L(PPh_3)$**

| | L = $PBu_3$ | L = $P(OMe)_3$ | L = $P(OPh)_3$ |
|---|---|---|---|
| mol wt | 628.6 | 538.4 | 736.6 |
| space group | $P\bar{1}$ | $P2_1/a$ | $P2_1/c$ |
| cell constants | | | |
| *a*, Å | 10.394 (6) | 16.519 (9) | 18.995 (9) |
| *b*, Å | 10.959 (6) | 10.241 (7) | 9.7171 (4) |
| *c*, Å | 17.638 (9) | 16.658 (9) | 21.176 (9) |
| α, deg | 71.33 (4) | | |
| β, deg | 76.09 (4) | 111.60 (4) | 111.90 (4) |
| γ, deg | 63.73 (4) | | |
| cell vol, $Å^3$ | 1695.2 | 2620.2 | 3626.5 |
| molecules/unit cell | 2 | 4 | 4 |
| ρ(calcd), g $cm^{-3}$ | 1.23 | 1.40 | 1.35 |
| μ(calcd), $cm^{-1}$ | 4.3 | 5.4 | 4.03 |
| radiation[a] | Mo Kα | Mo Kα | Mo Kα |
| scan width, deg | 0.85 + 0.2 tan θ | 0.8 + 0.2 tan θ | 0.8 + 0.2 tan θ |
| std reflctns | (008)(200) | (004)(200) | (006)(600) |
| decay of stds | <1% | ±2% | <2% |
| reflctns measd[b] | 3200 | 1900 | 3872 |
| range (θ) | 0–20 | 1–18 | 0–20 |
| obsd reflctns | 2353 | 1255 | 2456 |
| no. of parameters varied | 220 | 211 | 271 |
| GOF | 2.41 | 5.37 | 2.59 |
| *R* | 0.0883 | 0.071 | 0.057 |
| $R_w$ | 0.092 | 0.102 | 0.057 |

[a] Monochromated (graphite). [b] ω–2θ scan; only unique octants measured.

effervescence upon addition of the ligand to the solution. The reactions were stopped by the addition of 100 mL of pentane which caused the formation of a yellow precipitate. This solid, $Et_4N[LCr(CO)_4Cl]$, was washed several times with 20-mL portions of pentane to remove all traces of excess ligand and then dried in vacuo.

**Preparation of *trans*-$Cr(CO)_4LPPh_3$ (L = $PBu_3$, $P(OMe)_3$, and $P(OPh)_3$).** Approximately 10 mL of deoxygenated EtOH was added to a Schlenk flask containing 1.0 g of $Et_4N[LCr(CO)_4Cl]$ (~1.9 × $10^{-3}$ mol). To this mixture was added a 10-mL $CH_2Cl_2$ solution containing 0.5 g of $PPh_3$ (1.9 × $10^{-3}$ mol). After being stirred under argon for 1 h, the originally orange solution turned green yellow. Solvent removal gave a green-yellow solid which was extracted with hexane. This hexane solution containing $Cr(CO)_4LPPh_3$ was filtered, and the solvent was pumped off, giving a yellow solid which was recrystallized from $CH_2Cl_2$/EtOH. The yellow crystals were washed with pentane then dried in vacuo.

**$Cr(CO)_4(PBu_3)(PPh_3)$:** mp 141–142 °C decomposes without melting (reported 140–142 °C decomposes);[20] IR (hexane) (CO) 1882 (s), 1931 (w), 2004 (w) $cm^{-1}$. Anal. Calcd: Cr, 8.3; P, 9.9; C, 65.0; H, 6.7. Found: Cr, 8.0; P, 9.9; C, 65.1; H, 6.9.

**$Cr(CO)_4(P(OMe)_3)(PPh_3)$:** mp 132–133 °C; IR (hexane): ν(CO) 1914 (s), 1958 (w), 2023 (w), $cm^{-1}$. Anal. Calcd: Cr, 7.1; P, 8.4; C, 65.2; H, 4.1. Found: Cr, 7.0; P, 8.3, C, 65.1; H, 4.2.

The crystallographic data for the three complexes are presented in Table I and the fractional coordinates are given in Tables II–IV.

## Results

The molecular structure of each complex, as shown in Figures 1–3, has essentially octahedral coordination around the chromium with typical Cr–C and C–O bonds for the carbonyls. Selected bond distances and angles are given in Tables V and VI; the full listing is provided in the supplemental data. The geometry around phosphorus is typical of that seen for coordinated phosphines and phosphites. Thus the structural determinations show no unusual interactions and no gross structural differences for the three complexes.

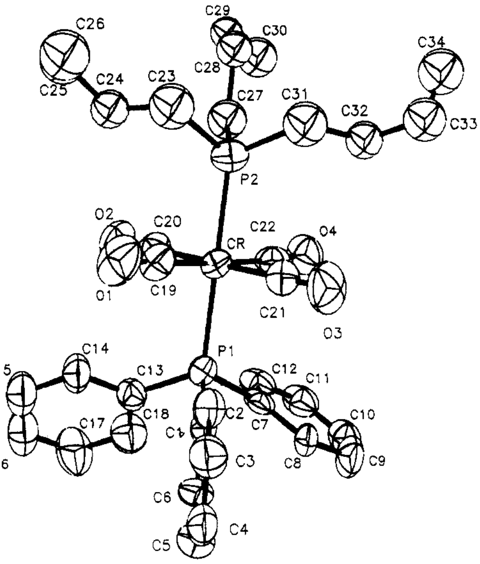


**Figure 1.** The molecular structure of *trans*-$Cr(CO)_4PBu_3(PPh_3)$ including the labeling.

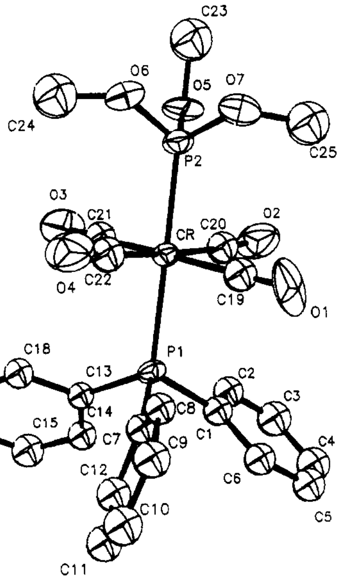


**Figure 2.** The molecular structure of *trans*-$Cr(CO)_4P(OMe)_3(PPh_3)$ including the labeling.

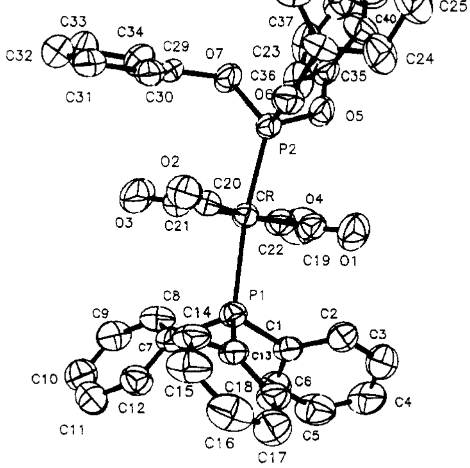


**Figure 3.** The molecular structure of *trans*-$Cr(CO)_4P(OPh)_3(PPh_3)$.

---

(20) Grim, S. O.; Wheatland, D. A.; McAllister, P. R. *Inorg. Chem.* **1968**, *7*, 161.

**Table II. Fractional Coordinates for *trans*-$Cr(CO)_4PBu_3PPh_3$**

| atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Cr | −0.0237 (2) | 0.2258 (2) | 0.7473 (1) |
| P(1) | 0.1515 (3) | 0.1496 (3) | 0.6414 (2) |
| P(2) | −0.1997 (4) | 0.3092 (4) | 0.8507 (2) |
| O(1) | −0.2258 (9) | 0.444 (1) | 0.6259 (6) |
| O(2) | −0.155 (1) | 0.023 (1) | 0.7562 (6) |
| O(3) | 0.178 (1) | 0.016 (1) | 0.8693 (6) |
| O(4) | 0.087 (1) | 0.437 (1) | 0.7515 (5) |
| C(19) | −0.149 (1) | 0.362 (1) | 0.6721 (8) |
| C(20) | −0.103 (1) | 0.099 (1) | 0.7530 (7) |
| C(21) | 0.100 (1) | 0.094 (1) | 0.8236 (8) |
| C(22) | 0.048 (1) | 0.356 (1) | 0.7485 (7) |
| C(1) | 0.254 (1) | −0.040 (1) | 0.6492 (6) |
| C(2) | 0.223 (1) | −0.138 (1) | 0.7147 (7) |
| C(3) | 0.300 (1) | −0.285 (1) | 0.7190 (8) |
| C(4) | 0.407 (1) | −0.326 (1) | 0.6561 (8) |
| C(5) | 0.437 (1) | −0.228 (1) | 0.5903 (8) |
| C(6) | 0.358 (1) | −0.084 (1) | 0.5853 (7) |
| C(7) | 0.296 (1) | 0.213 (1) | 0.6209 (6) |
| C(8) | 0.434 (1) | 0.121 (1) | 0.6441 (7) |
| C(9) | 0.539 (1) | 0.179 (1) | 0.6333 (8) |
| C(10) | 0.506 (1) | 0.321 (1) | 0.5999 (8) |
| C(11) | 0.370 (1) | 0.411 (1) | 0.5781 (7) |
| C(12) | 0.263 (1) | 0.356 (1) | 0.5887 (7) |
| C(13) | 0.090 (1) | 0.199 (1) | 0.5429 (6) |
| C(14) | −0.029 (1) | 0.168 (1) | 0.5407 (7) |
| C(15) | −0.075 (1) | 0.195 (1) | 0.4648 (8) |
| C(16) | −0.006 (2) | 0.248 (1) | 0.3961 (9) |
| C(17) | 0.112 (2) | 0.278 (2) | 0.3955 (9) |
| C(18) | 0.159 (1) | 0.254 (1) | 0.4710 (8) |
| C(23) | −0.284 (1) | 0.504 (1) | 0.8272 (8) |
| C(24) | −0.403 (2) | 0.574 (2) | 0.892 (1) |
| C(25) | −0.473 (2) | 0.741 (2) | 0.859 (1) |
| C(26) | −0.382 (3) | 0.801 (3) | 0.836 (2) |
| C(27) | −0.146 (2) | 0.253 (2) | 0.9547 (9) |
| C(28) | −0.037 (2) | 0.309 (2) | 0.958 (1) |
| C(29) | 0.021 (4) | 0.245 (3) | 1.049 (2) |
| C(30) | −0.041 (4) | 0.321 (4) | 1.090 (2) |
| C(31) | −0.355 (2) | 0.256 (2) | 0.8814 (9) |
| C(32) | −0.446 (2) | 0.314 (2) | 0.816 (1) |
| C(33) | −0.600 (4) | 0.283 (4) | 0.852 (2) |
| C(34) | −0.576 (4) | 0.167 (4) | 0.889 (2) |

**Table III. Fractional Coordinates for *trans*-$Cr(CO)_4P(OMe)_3PPh_3$**

| atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Cr | 0.0403 (2) | 0.1282 (3) | 0.7855 (2) |
| P(1) | −0.0519 (3) | −0.0418 (5) | 0.7074 (3) |
| P(2) | 0.1265 (4) | 0.2901 (6) | 0.8639 (4) |
| O(1) | 0.146 (1) | −0.077 (2) | 0.909 (1) |
| O(2) | 0.167 (1) | 0.107 (2) | 0.695 (1) |
| O(3) | −0.056 (1) | 0.328 (2) | 0.650 (1) |
| O(4) | −0.069 (1) | 0.168 (2) | 0.894 (1) |
| O(5) | 0.1627 (8) | 0.378 (1) | 0.8046 (8) |
| O(6) | 0.0924 (9) | 0.391 (1) | 0.9167 (8) |
| O(7) | 0.2094 (9) | 0.257 (1) | 0.9488 (8) |
| C(19) | 0.105 (1) | −0.000 (3) | 0.865 (1) |
| C(20) | 0.116 (1) | 0.114 (2) | 0.729 (1) |
| C(21) | −0.021 (1) | 0.252 (2) | 0.700 (1) |
| C(22) | −0.028 (1) | 0.152 (2) | 0.850 (2) |
| C(1) | −0.157 (2) | −0.157 (2) | 0.660 (1) |
| C(2) | 0.028 (1) | −0.115 (2) | 0.593 (1) |
| C(3) | 0.067 (1) | −0.201 (2) | 0.556 (1) |
| C(4) | 0.079 (1) | −0.329 (2) | 0.583 (1) |
| C(5) | 0.055 (1) | −0.371 (2) | 0.645 (1) |
| C(6) | 0.013 (1) | −0.288 (2) | 0.687 (1) |
| C(7) | −0.101 (1) | −0.148 (2) | 0.765 (1) |
| C(8) | 0.931 (1) | −0.156 (2) | 0.856 (1) |
| C(9) | −0.108 (1) | −0.240 (2) | 0.895 (1) |
| C(10) | −0.178 (1) | −0.310 (2) | 0.850 (1) |
| C(11) | −0.211 (1) | −0.305 (2) | 0.763 (1) |
| C(12) | −0.173 (1) | −0.224 (2) | 0.720 (1) |
| C(13) | −0.150 (1) | 0.009 (2) | 0.617 (1) |
| C(14) | −0.177 (1) | −0.041 (2) | 0.535 (1) |
| C(15) | −0.255 (1) | 0.001 (2) | 0.473 (1) |
| C(16) | −0.306 (1) | 0.083 (2) | 0.494 (1) |
| C(17) | −0.285 (1) | 0.134 (2) | 0.576 (1) |
| C(18) | −0.206 (1) | 0.097 (2) | 0.639 (1) |
| C(23) | 0.219 (2) | 0.488 (2) | 0.841 (2) |
| C(24) | 0.017 (2) | 0.467 (3) | 0.879 (2) |
| C(25) | 0.280 (1) | 0.182 (2) | 0.937 (2) |

## Discussion

The complexes *trans*-$Cr(CO)_4PPh_3L$ (L = $P(OPh)_3$, $PBu_3$, and $P(OMe)_3$) can be prepared quite readily from $Cr(CO)_6$ by reactions 2–4.

$$Cr(CO)_6 + Et_4NCl\cdot H_2O \xrightarrow[\Delta,\ 4\ h]{\text{diglyme/THF}} Et_4N[Cr(CO)_5Cl] + CO \quad (2)$$

$$Et_4N[Cr(CO)_5Cl] + L \xrightarrow[\text{room temp}]{\text{THF}} Et_4N[LCr(CO)_4Cl] + CO \quad (3)$$

$$L = PBu_3\ (10\ \text{min}),\ P(OMe)_3\ (30\ \text{min}),\ P(OPh)_3\ (1^1/_2\ \text{h})$$

$$Et_4N[LCr(CO)_4Cl] + L' \xrightarrow[\text{room temp, 1 h}]{EtOH/CH_2Cl_2} trans\text{-}Cr(CO)_4LL' + Et_4NCl \quad (4)$$

$$L' = PPh_3$$

The three structure determinations reported here for *trans*-$Cr(CO)_4PPh_3(P(OMe)_3)$, *trans*-$Cr(CO)_4PPh_3(P(OPh)_3)$, and *trans*-$Cr(CO)_4PPh_3(PBu_3)$ compared to that of $Cr(CO)_5PPh_3$[2] offers a series of compounds to compare the influence of changes of the trans ligand on the structures of the complexes, a *trans influence*. Comparison of $Cr–PPh_3$ bond distances, Cr–CO bond distances, and $Ph_3P–Cr–CO$ bond angles are shown in Table VII. The change in $Cr–PPh_3$ bond length seems rather sensitive to the nature of the ligand trans to it, varying by more than 0.07 Å. The order of variation parallels closely the $\sigma$ donor strength of the trans ligand, with the stronger $\sigma$ donor giving a shorter $Cr–PPh_3$ bond. This suggests that $\pi$-bonding is quite important to binding of $PPh_3$ to Cr(0) in these complexes. A ligand which enhances the electron density along the $Cr–PPh_3$ bond axis strengthens the $Cr–PPh_3$ bond. The effect of this bond shortening on reactivity will be discussed in a later paragraph. There is very little change in the $Ph_3P–Cr–CO$ bond angle for the different ligands, suggesting minimal steric interactions in these trans-substituted complexes.

There appears to be a trans influence on $Cr-P(OPh)_3$ bonds also as shown by the data in Table IX. For the series, *trans*-$Cr(CO)_4LP(OPh)_3$ the $Cr-P(OPh)_3$ bond lengths are as follows: L = $PPh_3$, $Cr-P(OPh)_3$ = 2.228 Å; L = $P(OPh)_3$, $Cr-P(OPh)_3$ = 2.252 Å; and L = CO, $Cr-P(OPh)_3$ = 2.309 Å. The shorter bond for the stronger donor in the trans position is consistent with $P(OPh)_3$ having a significant component of $\pi$-bonding.

One of the most interesting comparisons arises from a comparison of the structural data with the rates of reaction (eq 5). The details of the kinetic reactions have been

$$Cr(CO)_4PPh_3L + CO \rightarrow Cr(CO)_5L + PPh_3 \quad (5)$$

reported,[16] but the comparison between rate constant for $PPh_3$ dissociation and $Cr–PPh_3$ bond length is shown in Table VIII. There is perhaps an inverse correlation, but one can safely state that the $Cr–PPh_3$ bond length does not provide a measure of the rate of $PPh_3$ dissociation. Thus the effect of L on rate of dissociation is a result of transition-state effects, not ground-state effects.

A number of Cr–P bond lengths are now known. The complexes reported in this paper allow direct comparison

Table IV. Fractional Coordinates for *trans*-$Cr(CO)_4P(OPh)_3PPh_3$

| atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Cr | 0.26781 (6) | 0.7766 (1) | 0.27385 (6) |
| P(1) | 0.3602 (1) | 0.6584 (2) | 0.3675 (1) |
| P(2) | 0.1946 (1) | 0.8962 (2) | 0.1834 (1) |
| O(1) | 0.3743 (3) | 1.0203 (7) | 0.3029 (3) |
| O(2) | 0.1931 (3) | 0.9361 (6) | 0.3549 (3) |
| O(3) | 0.1496 (4) | 0.5528 (7) | 0.2522 (4) |
| O(4) | 0.3320 (4) | 0.6256 (8) | 0.1816 (3) |
| O(5) | 0.2251 (3) | 0.9127 (6) | 0.1225 (2) |
| O(6) | 0.1864 (3) | 1.0558 (5) | 0.2020 (2) |
| O(7) | 0.1082 (2) | 0.8534 (6) | 0.1362 (2) |
| C(19) | 0.3358 (4) | 0.9237 (9) | 0.2914 (4) |
| C(20) | 0.2221 (4) | 0.8715 (9) | 0.3255 (4) |
| C(21) | 0.1943 (5) | 0.6367 (9) | 0.2602 (4) |
| C(22) | 0.3088 (4) | 0.6832 (9) | 0.2169 (4) |
| C(1) | 0.4482 (4) | 0.6155 (8) | 0.3540 (4) |
| C(2) | 0.4832 (5) | 0.712 (1) | 0.3288 (4) |
| C(3) | 0.5510 (5) | 0.682 (1) | 0.3183 (5) |
| C(4) | 0.5817 (6) | 0.554 (1) | 0.3351 (5) |
| C(5) | 0.5493 (5) | 0.458 (1) | 0.3588 (5) |
| C(6) | 0.4815 (5) | 0.4864 (9) | 0.3699 (4) |
| C(7) | 0.3330 (4) | 0.4916 (8) | 0.3916 (4) |
| C(8) | 0.3007 (4) | 0.3922 (9) | 0.3415 (4) |
| C(9) | 0.2798 (5) | 0.2643 (9) | 0.3579 (4) |
| C(10) | 0.2927 (5) | 0.231 (1) | 0.4242 (4) |
| C(11) | 0.3251 (5) | 0.3261 (9) | 0.4743 (5) |
| C(12) | 0.3454 (4) | 0.4574 (9) | 0.4586 (4) |
| C(13) | 0.3946 (4) | 0.7532 (8) | 0.4480 (3) |
| C(14) | 0.3414 (5) | 0.7971 (8) | 0.4748 (4) |
| C(15) | 0.3650 (5) | 0.8718 (9) | 0.5360 (4) |
| C(16) | 0.4403 (5) | 0.901 (1) | 0.5693 (5) |
| C(17) | 0.4925 (5) | 0.8574 (9) | 0.5445 (4) |
| C(18) | 0.4709 (4) | 0.7829 (8) | 0.4839 (4) |
| C(23) | 0.1633 (5) | 0.1626 (9) | 0.1543 (4) |
| C(24) | 0.2176 (5) | 1.252 (1) | 0.1505 (5) |
| C(25) | 0.1956 (6) | 1.359 (1) | 0.1031 (5) |
| C(26) | 0.1200 (6) | 1.378 (1) | 0.0639 (6) |
| C(27) | 0.0679 (7) | 1.291 (1) | 0.0689 (6) |
| C(28) | 0.0860 (6) | 1.179 (1) | 0.1152 (5) |
| C(29) | 0.0524 (4) | 0.8145 (8) | 0.1602 (4) |
| C(30) | 0.0394 (4) | 0.8848 (8) | 0.2105 (4) |
| C(31) | −0.0192 (4) | 0.8414 (9) | 0.2313 (4) |
| C(32) | −0.0636 (5) | 0.734 (1) | 0.1986 (4) |
| C(33) | −0.0512 (5) | 0.665 (1) | 0.1490 (5) |
| C(34) | 0.0078 (5) | 0.7047 (9) | 0.1282 (4) |
| C(35) | 0.1881 (4) | 0.8889 (8) | 0.0528 (4) |
| C(36) | 0.1696 (4) | 0.7583 (9) | 0.0293 (4) |
| C(37) | 0.1356 (5) | 0.737 (1) | −0.0410 (5) |
| C(38) | 0.1214 (5) | 0.844 (1) | −0.0841 (5) |
| C(39) | 0.1407 (5) | 0.971 (1) | −0.0620 (5) |
| C(40) | 0.1741 (5) | 0.998 (1) | 0.0087 (4) |

Table V. Selected Bond Distances for *trans*-$Cr(CO)_4LPPh_3$

| | distance, Å | | |
|---|---|---|---|
| atoms | L = $PBu_3$ | L = $P(OMe)_3$ | L = $P(OPh)_3$ |
| Cr-P(1) | 2.349 (4) | 2.364 (6) | 2.395 (2) |
| Cr-P(2) | 2.344 (4) | 2.261 (6) | 2.228 (2) |
| Cr-C(19) | 1.88 (1) | 1.89 (3) | 1.868 (9) |
| Cr-C(20) | 1.87 (1) | 1.83 (2) | 1.874 (9) |
| Cr-C(21) | 1.87 (1) | 1.90 (3) | 1.89 (1) |
| Cr-C(22) | 1.89 (1) | 1.84 (3) | 1.89 (1) |
| C(19)-O(1) | 1.15 (1) | 1.12 (2) | 1.158 (8) |
| C(20)-O(2) | 1.16 (1) | 1.18 (2) | 1.157 (8) |
| C(21)-O(3) | 1.14 (1) | 1.13 (2) | 1.144 (9) |
| C(22)-O(4) | 1.15 (1) | 1.18 (2) | 1.145 (9) |

Table VI. Selected Bond Angles for *trans*-$Cr(CO)_4LPPh_3$

| | angles, deg | | |
|---|---|---|---|
| atoms | L = $PBu_3$ | L = $P(OMe)_3$ | L = $P(OPh)_3$ |
| P(1)-Cr-P(2) | 178.2 (2) | 178.0 (3) | 172.54 (9) |
| P(1)-Cr-C(19) | 91.1 (4) | 87.5 (7) | 87.9 (2) |
| P(1)-Cr-C(20) | 91.6 (4) | 94.5 (7) | 96.2 (2) |
| P(1)-Cr-C(21) | 89.9 (3) | 91.2 (6) | 93.0 (2) |
| P(1)-Cr-C(22) | 92.3 (3) | 90.3 (7) | 87.1 (2) |
| P(2)-Cr-C(19) | 88.8 (4) | 91.8 (7) | 86.3 (2) |
| P(2)-Cr-C(20) | 89.7 (4) | 87.4 (7) | 88.2 (2) |
| P(2)-Cr-C(21) | 90.2 (4) | 89.6 (6) | 93.2 (2) |
| P(2)-Cr-C(22) | 86.4 (3) | 87.8 (7) | 88.6 (2) |
| C(19)-Cr-C(20) | 89.9 (5) | 89.2 (9) | 86.8 (3) |
| C(19)-Cr-C(21) | 178.6 (5) | 176 (1) | 174.8 (3) |
| C(19)-Cr-C(22) | 90.9 (5) | 90 (1) | 94.3 (3) |

Table VII. Comparison of Selected Parameters in the Structures of *trans*-$Cr(CO)_4PPh_3L$ (L = $P(OMe)_3$, $P(OPh)_3$, $PBu_3$, and CO)

| L | Cr-$PPh_3$, Å | Cr-CO(av), Å | $Ph_3P$-Cr-CO, deg |
|---|---|---|---|
| $PBu_3$ | 2.349 (4) | 1.87 | 91.2 |
| $P(OMe)_3$ | 2.364 (6) | 1.87 | 91.0 |
| $P(OPh)_3$ | 2.395 (2) | 1.88 | 91.2 |
| CO[a] | 2.422 (1) | 1.88 | 91.6 |

[a] Reference 5.

Table VIII. Comparison of the Rate Constant at 130 °C for $PPh_3$ Dissociation from *trans*-$Cr(CO)_4PPh_3L$ with Cr-$PPh_3$ Bond Length (Å)

| L | Cr-$PPh_3$ bond length | rate const, $s^{-1}$ |
|---|---|---|
| $PBu_3$ | 2.349 (4) | $2.35 \times 10^{-1}$ |
| $P(OPh)_3$ | 2.395 (2) | $1.34 \times 10^{-2}$ |
| $P(OMe)_3$ | 2.364 (6) | $8.08 \times 10^{-3}$ |
| CO | 2.422 (1) | $1.0 \times 10^{-4}$ |

Table IX. Bond Distances (Å) for Selected Phosphine and Phosphite Derivatives of $Cr(CO)_6$

| | bond dist | ref |
|---|---|---|
| Cr-$PR_3$ | | |
| Cr-$PPh_3$ in $Cr(CO)_4PPh_3(PBu_3)$ | 2.349 | this work |
| Cr-$PPh_3$ in *trans*-$Cr(CO)_4PPh_3(P(OMe)_3)$ | 2.364 | this work |
| Cr-$PPh_3$ in *trans*-$Cr(CO)_4PPh_3(P(OPh)_3)$ | 2.395 | this work |
| Cr-$PPh_3$ in $Cr(CO)_5PPh_3$ | 2.422 | 5 |
| Cr-$PBu_3$ in *trans*-$Cr(CO)_4PPh_3(PBu_3)$ | 2.344 | this work |
| Cr-$PEt_3$ in *trans*-$Cr(CO)_3(PEt_3)_3$ | 2.429 | 8 |
| Cr-$PH_3$ in *fac*-$Cr(CO)_3(PH_3)_3$ | 2.346 | 9 |
| average | 2.377 | |
| Cr-$P(OR)_3$ | | |
| Cr-$P(OMe)_3$ in *trans*-$Cr(CO)_4PPh_3(P(OMe)_3)$ | 2.261 | this work |
| Cr-$P(OPh)_3$ in *trans*-$Cr(CO)_4PPh_3(P(OPh)_3)$ | 2.228 | this work |
| Cr-$P(OPh)_3$ in *trans*-$Cr(CO)_4(P(OPh)_3)_2$ | 2.252 | 12 |
| Cr-$P(OPh)_3$ in $Cr(CO)_5P(OPh)_3$ | 2.309 | 5 |
| average | 2.263 | |

of the bond lengths of two different phosphorus ligands in the same complex. The striking feature of this comparison is the marked shortness of chromium–phosphite bonds in comparison to chromium–phosphine bands. The direct comparison in the same complex is complimented by comparison of different complexes as shown in Table IX. On the average a chromium–phosphite bond is 0.11 Å shorter than a chromium–phosphine bond. This is consistent with the bond strengths determined from reaction chemistry.[17,18,21] Electronic and steric factors must both be involved in the shorter chromium–phosphite bonds.

The three structures reported in this paper indicate a significant *trans influence* on the bonding of $PPh_3$ to chromium(0) with a stronger donor ligand in the trans

---

(21) Manzer, L. E.; Tolman, C. A. *J. Am. Chem. Soc.* **1976**, *97*, 1955.

position leading to a shorter Cr–$PPh_3$ bond. Thus a significant component of π bonding to the full bond between chromium and triphenylphosphine is indicated.

**Acknowledgment.** Support of this work by the National Science Foundation and donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. J.D.A. acknowledges the Alfred P. Sloan Foundation and helpful discussions with M. R. Churchill.

**Registry No.** *trans*-$Cr(CO)_4PPh_3(PBu_3)$, 17652-69-6; *trans*-$Cr(CO)_4PPh_3(P(OMe)_3)$, 95341-15-4; *trans*-$Cr(CO)_4PPh_3(P(OPh)_3)$, 82613-90-9; $Et_4N[(PBu_3)Cr(CO)_4Cl]$, 95218-76-1; $Et_4N[(P(OMe)_3Cr(CO)_4Cl]$, 95341-14-3; $Et_4N[(P(OPh)_3Cr(CO)_4Cl]$, 95218-78-3; $Et_4N[Cr(CO)_5Cl]$, 14780-95-1; $Cr(CO)_6$, 13007-92-6; Cr, 7440-47-3; P, 7723-14-0.

**Supplementary Material Available:** Tables of thermal parameters, bond distances and angles, and observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

---

# Nucleophilic Addition to Coordinated Cycloheptatriene: A Mechanistic and Structural Study

Ephraim D. Honig, Meng Quin-jin,[1a] Ward T. Robinson,[1b] Paul G. Williard, and
Dwight A. Sweigart*

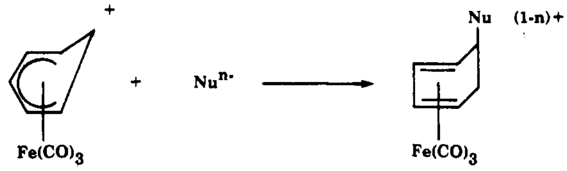
*Department of Chemistry, Brown University, Providence, Rhode Island 02912*

*Received September 10, 1984*

The addition of phosphorus and nitrogen donor nucleohiles (Nu) to the cycloheptatriene ring in $(C_7H_8)Mn(CO)_2L^+$ (1; L = CO, $PPh_3$) yields $(exo\text{-}NuC_7H_8)Mn(CO)_2L^+$. *N,N*-Dimethylaniline undergoes an electrophilic aromatic substitution reaction with 1 (L = CO) to give $(exo\text{-}Me_2NC_6H_4C_7H_8)Mn(CO)_3$, in which the carbon para to the $NMe_2$ substituent is bonded to the $C_7H_8$ ring. Kinetic studies of the addition reactions show that 1 (L = CO) is an extremely reactive electrophile and that the relative nucleophilic reactivities are the same as found for other, less reactive, organometallic substrates as well as for free carbonium ions. A single-crystal X-ray analysis of $[(exo\text{-}PPh_3C_7H_8)Mn(CO)_3]BF_4$ showed that it crystallizes in the monoclinic space group $P2_1/c$ with $a$ = 9.595 (3) Å, $b$ = 14.580 (4) Å, $c$ = 19.574 (6) Å, $\beta$ = 107.23 (8)°, and $R_w$ = 0.0448. The structure shows that the dienyl carbons (C4–C5–C6–C7–C8) are planar and form a dihedral angle of 45.8° with the nonbonded plane (C10–C9–C8–C4). The carbon skeleton defining the cycloheptadienyl ring possesses approximate $C_s$ symmetry.

## Introduction

The electrophilic activation of normally unreactive π-hydrocarbons as well as the stabilization of certain highly reactive carbonium ions (e.g., $C_6H_7^+$, $C_7H_7^+$) can frequently be accomplished by coordination to a transition-metal center.[2] This chemistry has attracted considerable attention due to its applications in organic synthesis. The best known reactions involving *cyclic* π-hydrocarbons are the addition of nucleophiles to the ring in (cyclohexadienyl)$Fe(CO)_3^+$ (eq 1)[3-6] and (arene)$Cr(CO)_3$[7] to give (diene)$Fe(CO)_3$ and (dienyl)$Cr(CO)_3$ complexes. The functionalized diene or dienyl ligands can then be removed from the metal by a variety of oxidizing procedures. While (cyclohexadienyl)$Fe(CO)_3^+$ complexes are reactive toward even mild nucleophiles, only the most powerful carbanions react successfully with (arene)$Cr(CO)_3$. However, due in part to the positive charge, cationic (arene)$Mn(CO)_3^+$ complexes react smoothly with relatively mild carbon donors,[8] and in some cases the addition of two nucleophiles to the arene is possible[9,10] starting with (arene)$Mn(CO)_3^+$.



(1)

Nucleophilic addition to the π-hydrocarbon ring in (ring)$ML_n^{m+}$ is closely related to additions to free carbonium ions. The latter reaction involves simple electrophile–nucleophile (E–N) combination, whereas the organometallic reactions also involve cleavage of a metal–metal bond, i.e., are really $S_N2$ reactions in which the leaving group ($ML_n$) remains bonded to the periphery of the molecule. Ritchie[11] has found that oxygen and nitrogen donor nucleophiles add to free carbonium ions (trityl, tropylium, pyronin, etc.) such that the relative nucleophilic reactivity is electrophile independent. Furthermore, this may also be true for atack on esters and activated arenes, providing the leaving group departure is not rate deter-

---

[1] Permanent addresses: (a) Department of Chemistry, Nanjing University, Nanjing, China. (b) Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

[2] Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525.

[3] Birch, A. J. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 107.

[4] Birch, A. J.; Kelly, L. F.; Narula, A. S. *Tetrahedron* **1982**, *38*, 1813.

[5] Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463.

[6] Pearson, A. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8, Chapter 58.

[7] Semmelhack, M. F.; Garcia, J. L.; Cortes, D.; Farina, R.; Hong, R.; Carpenter, B. K. *Organometallics* **1983**, *2*, 467 and references therein.

[8] Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1982**, *1*, 1053.

[9] Chung, Y. K.; Choi, H. S.; Swiegart, D. A.; Connelly, N. G. *J. Am. Chem. Soc.* **1982**, *104*, 4245.

[10] Chung, Y. K.; Honig, E. D.; Robinson, W. T.; Sweigart, D. A.; Connelly, N. G.; Ittel, S. D. *Organometallics* **1983**, *2*, 1479.

[11] Ritchie, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 3573 and references therein.

0276-7333/85/2304-0871$01.50/0