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Kinetics and mechanisms of the ligand substitution of $(\eta^5\text{-}C_9H_7)M(CO)_4$, where M = Nb or Ta, and a reinvestigation of the kinetics of $(\eta^5\text{-}C_5H_5)M(CO)_4$. Molecular structure of $(\eta^5\text{-}C_5H_5)Nb(Co)_3[P(C_6H_5)_3]$

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday

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Abstract

Kinetic studies were performed for CO substitution reactions of $(\eta^5\text{-}C_5H_5)M(CO)_4$ and $(\eta^5\text{-}C_9H_7)M(CO)_4$ (where M = Nb, Ta) with phosphines and phosphites. Niobium derivatives were found to undergo ligand exchange at higher rates than tantalum, and indenyl derivatives exchanged faster than cyclopentadienyl derivatives. The cyclopentadienyl compounds were found to react by a dissociative or dissociative interchange mechanism as opposed to an associative mechanism as suggested by an earlier kinetic study. The indenyl compounds were found to predominantly react by an associative mechanism. Rate and thermodynamic data indicate that the indenyl effect is operative in these Group V compounds. The molecular structure of $(\eta^5\text{-}C_5H_5)Nb(CO)_3[P(C_6H_5)_3]\cdot 0.25CH_2Cl_2$ was determined: $P\bar{1}$, $a = 10.817(2)$, $b = 12.403(2)$, $c = 18.962(3)$ Å, $\alpha = 100.901(13)$, $\beta = 104.695(10)$, $\gamma = 103.52(2)°$, $V = 2307.6(7)$ Å^3, $Z = 4$, $R_F = 3.36$. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Molecular structure; Kinetics; Substitution reactions

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1. Introduction

The ligand exchange kinetics of cyclopentadienyl (Cp) and indenyl (Ind) metal carbonyl compounds have been investigated extensively. It has been found that $CpM(CO)_n$ compounds may react by either associative or dissociative mechanisms, while $IndM(CO)_n$ compounds tend to favor associative mechanisms [1–3]. The term indenyl effect was coined by Basolo [4] to describe the rate enhancement found for indenyl compounds and attributed to the ability of this ligand to undergo an η^5 to η^3 haptotropic rearrangement thus facilitating ligand association.

It has been reported that $CpV(CO)_4$ undergoes substitution of CO by phosphines by a dissociative mechanisms [5], while the analogous Nb and Ta compounds are reported to react by both associative and dissociative mechanisms [6]. It was found that reactivity of the Group V series increases in the order V > Nb > Ta, in contrast to the expectations of the triad rule that would predict the order V < Nb > Ta. In the case of vanadium, substitution of the cyclopentadienyl ligand by the indenyl ligand did not change the dissociative mechanism of the reaction but did increase the constant of dissociation by a factor of 13 (at 100°C) [7]. The fact that the indenyl compound did not undergo exchange by an associative pathway was attributed to the small size of the V atom and an unusually high degree of crowding to be expected in the putative associative intermediate $(\eta^3\text{-}C_9H_7)V(CO)_4L$.

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We have reported recently the first syntheses of a number of ring substituted niobium and tantalium cyclopentadienyl carbonyl compounds including the indenyl derivatives via intermediates pioneered by Professor Calderazzo, and his coworkers [8]. These compounds have provided us with the opportunity to extend the investigation of the indenyl effect into the lower Group V elements. In preparation for our investigation of the indenyl derivatives, we reexamined the kinetics of the cyclopentadienyl compounds and have found evidence that is more suggestive of a dissociative, or dissociative interchange mechanism for these reactions. The results of these kinetics studies for the cyclopentadienyl and indenyl niobium and tantalum carbonyl compounds are reported in this paper.

2. Experimental

2.1. General procedures

The indenyl niobium/tantalum tetracarbonyl and cyclopentadienyl niobium/tantalum tetracarbonyl complexes used in this work are air and light sensitive in solution. All manipulations of these complexes were carried out under an atmosphere of N_2 or Ar, using standard Schlenk or glove box techniques. Solutions were protected routinely from light and sample preparation for the indenyl derivatives was carried out in the dark using red light. Hexadecane was distilled under vacuum and stored under nitrogen. The synthesis and characterization of the compounds used in these studies have been reported previously [9].

Infrared spectra were recorded on a Perkin–Elmer spectrum 1000 FT-IR spectrometer using 0.5 mm path length NaCl cells. Before each spectral measurement, the cell was purged with nitrogen and sealed with rubber septa to avoid air contamination. A high temperature bath was constructed from a 500-ml beaker wrapped with asbestos tape and filled with silicon oil. The temperature of this bath was regulated by a Cole–Parmer hot plate/stirrer equipped with a temperature controller. When shielded from laboratory air currents, this system was able to maintain temperatures within ± 0.2°C.

2.2. Kinetic studies

All kinetic experiments were run under pseudo-first-order conditions with at least a tenfold excess of ligand. A solution of ligand in hexadecane (4.7 ml) was equilibrated in the constant temperature bath. When the solution had reached thermal equilibrium, a solution of metal complex in hexadecane (0.3 ml) was added. Stock metal solutions were prepared by dissolving 10–15 mg of metal compound in 2 ml of hexadecane. These stock solutions were used for each kinetic run within a series. The reactions were monitored by IR spectroscopy using the area of the strong asymmetric carbonyl stretching band as the quantitative probe. All data points represent the average of at least three experimental runs.

2.3. Crystallographic structural determination

Crystal, data collection and refinement parameters are given in Table 5.

The diffraction data were consistent for space groups $P1$ and $P\bar{1}$ The E-statistics strongly suggested the centrosymmetric space group $P\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved using direct-methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. Absorption corrections were not required because the variation in the integrated ψ-scan intensities was less then 10%. There are two symmetry independent, but chemically equivalent molecules of the complex in the asymmetric unit. There is also a half of a solvate dichloromethane molecule disordered over an inversion center in the asymmetric unit. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXYL (version 5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI).

3. Results and discussion

The reactions of $CpM(CO)_4$ (M = Nb, Ta) with tributylphosphine, PBu_3, in hexadecane proceeded according to Eq. (1) to give monosubstituted products.

$$CpM(CO)_4 + PBu_3 \rightarrow CpM(CO)_3PBu_3 + CO \qquad (1)$$

No decomposition was observed over the time of the kinetics studies and the formation of traces of disubstituted material toward the end of the reaction times had no effect on the ability to measure the decreasing concentration of $CpM(CO)_4$. Values of k_{obs} were obtained by monitoring the decrease over time of the area of the strong asymmetric carbonyl stretching band of the starting materials. A representative example of the IR spectra recorded during the kinetic reactions is shown in Fig. 1. Plots of k_{obs} versus [L] (Fig. 2), are non-linear and show a distinct change in the relationship between k_{obs} and [L] with increasing ligand concentration. As this behavior is not consistent with the earlier report [6], a scrupulous effort was made to identify and reduce or eliminate any possible sources of error. To the best of our ability, the experimental methods used in these studies duplicated those of the previous work.

As seen in Fig. 2, k_{obs} is strongly dependent upon [L] at low ligand concentration and less dependent on [L] at high ligand concentration. The rate law that best accommodates the observations is:

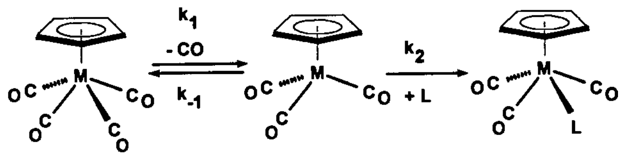
$$\text{Rate} = \frac{k_1 k_2[\text{L}][\text{CpM(CO)}_4]}{k_{-1} + k_2[\text{L}]}$$

The mechanism in this case (Scheme 1), involves a rapid pre-equilibrium with loss of CO to form a 16-electron intermediate, followed by reaction of this intermediate with L [2]. At low ligand concentration, this equation resembles a second order process, while at higher ligand concentrations the process becomes more independent of the ligand. The k_1 and k_{-1}/k_2 values obtained from these studies are summarized in Table 1 and the thermodynamic activation parameters are presented in Table 4.

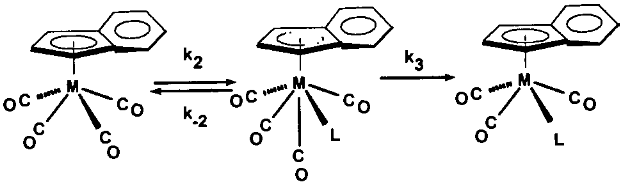
In contrast to the cyclopentadienyl derivatives, plots of k_{obs} versus [L] for reaction of the indenyl derivatives, indicate a simple linear dependence upon [L]. A non-zero intercept indicates a small contribution from a dissociative pathway (Table 2). This intercept is almost the same for $P(n\text{-BU})_3$ and $P(O\text{-}4\text{-MeC}_6H_4)_3$ (Fig. 3). The data for the reactions fit the rate law:

$$\text{Rate} = k_1 + k_2[\text{L}]$$

where $k_1 \ll k_2$ consistent with Scheme 2. Table 3 summarizes the first and second order rate constants for these reactions. Activation parameters are presented in Table 4.



Scheme 1. Dissociative mechanism for ligand exhange, M = Nb, Ta.



Scheme 2. Associative mechanism involving indenyl effect. Dissociative pathway is minor and is not illustrated.

Reaction of $CpNb(CO)_4$ with $P(C_6H_5)_3$ on a preparative scale permitted isolation of a sample of $CpNb(CO)_3[P(C_6H_5)_3]P(C_6H_5)_3$ was selected in this case because in our experience these derivatives form better crystals than $P(n\text{-Bu})_3$. Recrystallization from CH_2Cl_2–petroleum ether yielded deep red X-ray quality crystals. Crystallographic data are presented in Table 5 and selected bond lengths and angles are presented in Table 6. The two independent molecules in the asymmetric unit were identical chemically. The molecular structure of this compound (Fig. 4) exhibits the expected four-legged piano stool geometry. Nb–CO and C–O bond lengths for the carbonyl group *trans* to the triphenylphosphine ligand (C_6–O_6) are shorter and

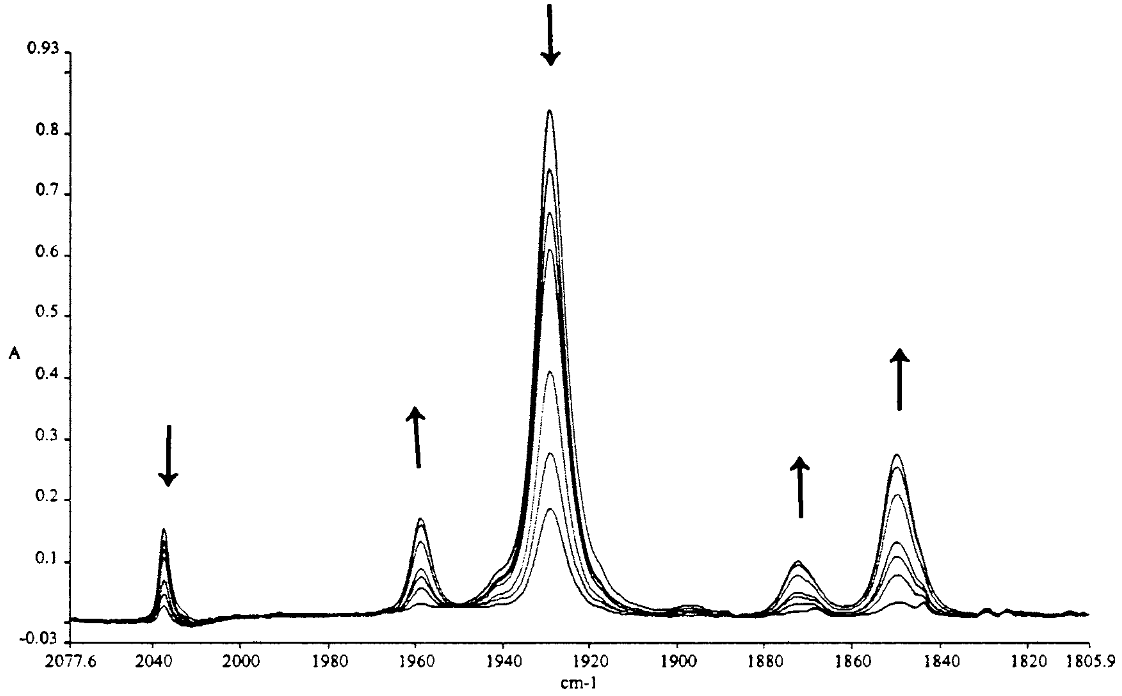


Fig. 1. Infrared spectral changes for the reaction between $CpNb(CO)_4$ and $P(n\text{-Bu})_3$ in hexadecane at 150°C.

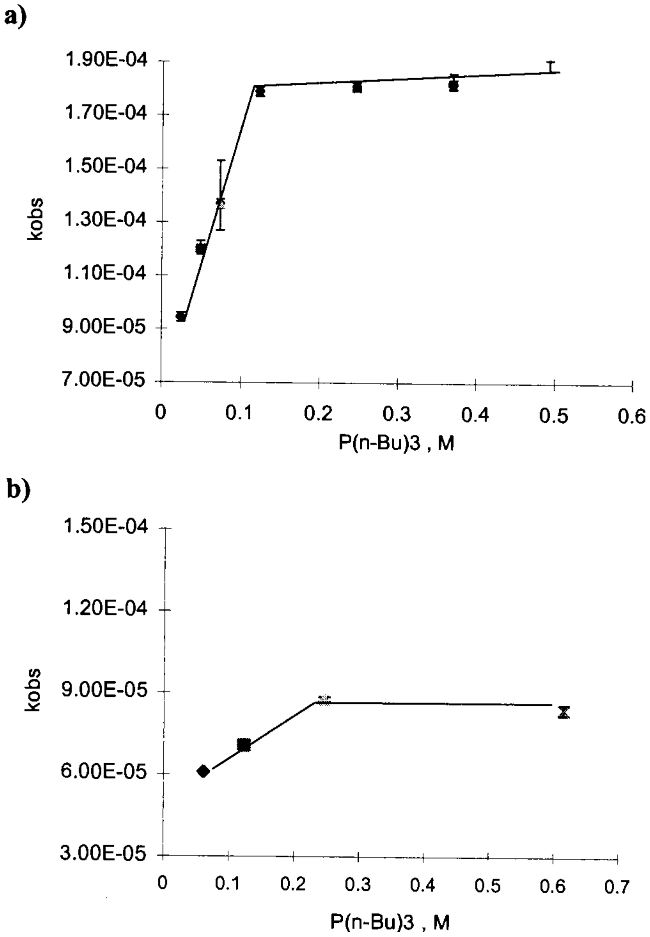


Fig. 2. (a) Plot of k_{obs} versus P(n-Bu)$_3$ concentration for the reaction of CpNb(CO)$_4$ (1.23E − 03 M) Wth P(n-Bu)$_3$ in hexadecane at 150°C. (b) Plot of k_{obs} versus P(n-Bu)$_3$ concentration for the reaction of CpTa(CO)$_4$ (1.23E − 03 M) with P(n-Bu)$_3$ in hexadecane at 190°C.

longer, respectively, than those *cis* to the phosphine reflecting the expected *trans* effect of the relatively weak phosphine π-acid.

4. Discussion

As noted in Section 1, Basolo and Freeman [6] have reported previously, kinetic studies of CpM(CO)$_4$, where M = Nb and Ta. In contrast to our results, their data suggested a rate law with both associative and dissociative components. To understand the differences between these two sets of results using essentially identical experimental methods, we note that our studies have had the luxury of large quantities of the niobium and tantalum compounds allowing us to carry out the kinetics measurements at a number of concentrations of L. These additional data points, particularly those at lower concentrations of L, made it clear that the true concentration dependence was more complex than the linear relationship reported earlier. Indeed, if similar points are selected from our data, it is possible to approximate the concentration dependence and thermodynamic parameters of the earlier work.

While the rate law derived from our data suggests that the reaction fits a dissociative mechanism profile, we note that the $\Delta S^{\ddagger}$ values are small suggesting that

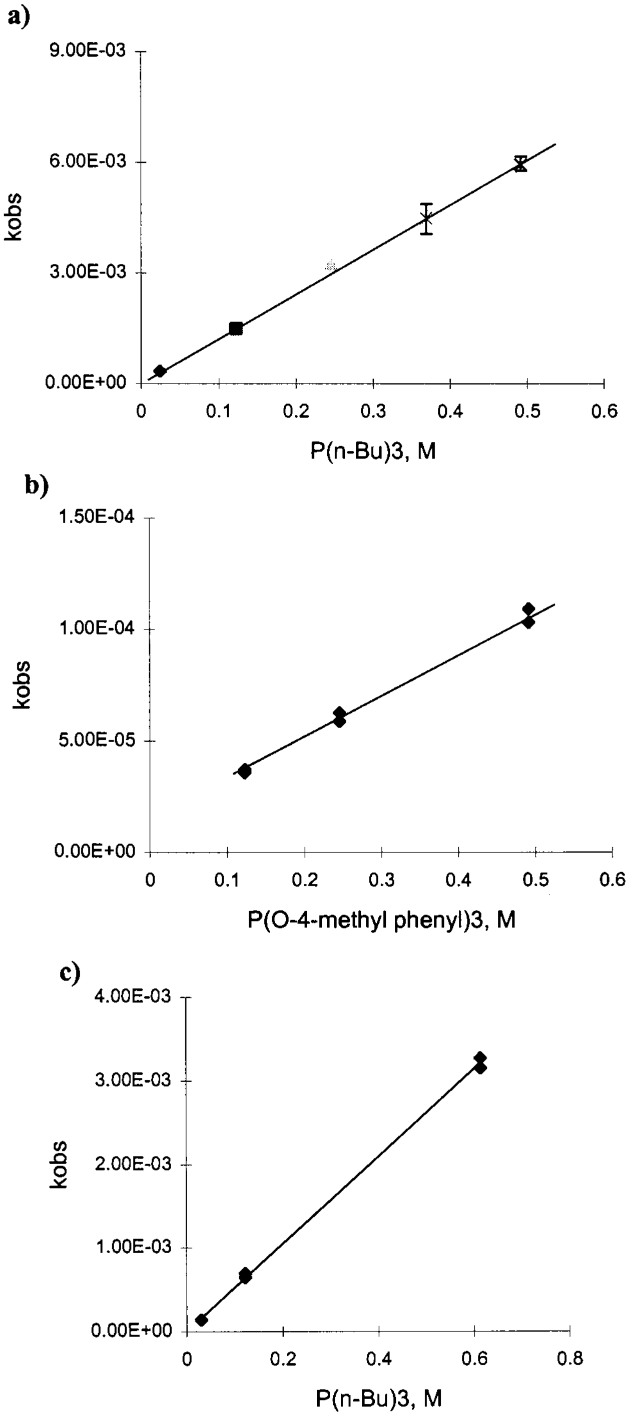


Fig. 3. (a) Plot of k_{obs} versus P(n-Bu)$_3$ concentration for the reaction of IndNb(CO)$_4$ (1.23E − 03 M) with P(n-BU)$_3$ in hexadecane at 100°C. (b) Plot of k_{obs} versus P(O-4-methyl phenyl)$_3$ concentration for the reaction of IndNb(CO)$_4$ (1.23E − 03 M) with P(O-4-methyl henyl) in hexadecane at 100°C. (c) Plot of k_{obs} versus PR$_3$ concentration for the reaction of IndTa(CO)$_4$ (1.23E − 03 M) with P(n-Bu), in hexadecane at 100°C.

Table 1
Forward k_1 and (k_{-1}/k_2) rate constants for the reaction of $CpM(CO)_4$ with $P(n\text{-}Bu)_3$ in hexadcane

Temperature (°C)	k_1	$(k_{-1}/k_2)\times 10^2$
CpNb(CO)$_4$		
140	0.629×10^4	1.86
150	2.00×10^4	2.87
160	4.12×10^4	0.67
170	14.0×10^4	0.58
CpTa(CO)$_4$		
185	5.34×10^5	1.97
190	9.19×10^5	3.16
195	13.5×10^5	0.393

Table 2
Rate constants (k_{obs}) for the reactions of $IndM(CO)_4$ (M = Nb, Ta) with $P(n\text{-}Bu)_3$ in hexadecane

Compound	Temperature (°C)	k_{obs}
$IndNb(CO)_4$	80	4.71×10^{-4}
	100	1.49×10^{-4}
	120	4.39×10^{-3}
$IndTa(CO)_4$	90	3.62×10^{-4}
	100	6.67×10^{-4}
	110	1.02×10^{-3}

Table 3
First (k_1) and second order (k_2) rate constants for the reactions of $IndM(CO)_4$ (M = Nb and Ta), with $P(n\text{-}Bu)_3$ and $P(O\text{-}4\text{-}tol)_3$ in hexadecane at 100°C

Compound	L	k_1 (diss)	k_2 (assoc)
$IndNb(CO)_4$	$P(n\text{-}Bu)_3$	8.22×10^{-5}	1.20×10^{-2}
$IndNb(CO)_4$	$P(O\text{-}4\text{-}tol)_3$	1.37×10^{-5}	1.88×10^{-4}
$IndTa(CO)_4$	$P(n\text{-}Bu)_3$	1.86×10^{-6}	5.23×10^{-3}

the actual mechanism is probably I_d. Basolo made a very similar observation in the ligand exchange reactions of $CpM(CO)_3(THF)$ [6].

Basolo and Freeman found that the second order rate constants of $CpNb(CO)_4$ increased in the order: $P(OPh)_3 < P(n\text{-}Bu)_3 < PMe_2Ph$ with the phosphite reaction showing small second order behavior (at 160°C). The cone angle for these three ligands increases in the order: 128, 132, and 136°. Considering the mechanism of the dissociative reaction, it is possible that steric crowding of the $CpM(CO)_3$ intermediate might make k_2 particularly sensitive to the size of the incoming ligand, thus for a larger ligand k_{-1} may be much larger than $k_2[L]$, making the equation indistinguishable from a second order process. We are initiating an expanded investigation of the kinetics of these compounds to examine the effects of incoming ligand size and basicity.

Ligand exchange by the indenyl derivatives of niobium and tantalum follow a simple rate law in which both associative and dissociative pathways are observed, with the associative pathway being dominant. k_2 for $P(n\text{-}Bu)_3$ is larger than that for $P(O\text{-}4\text{-}tol)_3$ consistent with an associative process in which the rate is dependent upon the basicity of the incoming ligand. The analogous vanadium compound has been found to react with $P(n\text{-}Bu)_3$ by a dissociative mechanism. The change in mechanism between vanadium and the heavier members of the triad may reflect the comparatively

Table 4
Kinetic parameters for reactions of $CpM(CO)_4$ and $IndM(CO)_4$ (M = Nb, Ta) with $P(n\text{-}Bu)_3$

Compound	ΔH (kJ mol^{-1})	ΔS (JK^{-1} mol^{-1})
$CpNb(CO)_4$	143 ± 1	17.2 ± 1.3
$CpTa(CO)_4$	148 ± 12	-7.40 ± 10.9
$IndNb(CO)_4$	61.1 ± 0.4	-137 ± 1
$IndTa(CO)_4$	58.2 ± 0.8	-152 ± 2

Table 5
Crystallographic data for $CpNb(CO)_3(PPh_3)$

Formula	$C_{26.25}H_{20.50}Cl_{0.50}NbO_3P$
Formula weight	525.53
Space group	$P\bar{1}$
a (Å)	10.817(2)
b (Å)	12.403(2)
c (Å)	18.962(3)
α (°)	100.901 (13)
β (°)	104.695 (10)
γ (°)	103.52(2)
V (Å^3)	2307.6(7)
Z	4
Crystal color	Red block
μ(Mo–K$_\alpha$) (cm^{-1})	6.74
Temperature (K)	248(2)
Radiation (Å)	Mo–K$_\alpha$ ($\lambda = 0.71073$)
$R(F)$ (%)	3.36
$R(wF^2)$, (%)	8.56

Table 6
Selected (Å) and angles (°) for $CpNb(CO)_3PPh_3$

Bond lengths			
Nb–C$_1$	2.395(4)	C$_1$–C$_2$	1.400(7)
Nb–C$_2$	2.426(6)	C$_2$–C$_3$	1.378(7)
Nb–C$_3$	2.440(4)	C$_3$–C$_4$	1.410(7)
Nb–C$_4$	2.415(6)	C$_1$–C$_5$	1.400(7)
Nb–C$_6$	2.036(4)	C$_6$–O$_6$	1.163(5)
Nb–C$_7$	2.057(5)	C$_7$–O$_7$	1.149(5)
Nb–C$_8$	2.050(4)	C$_8$–O$_8$	1.148(5)
Nb–P	2.578(10)		
Bond angles			
C$_6$–Nb–C$_7$	71.5(2)	C$_6$–Nb–C$_8$	70.9(2)
C$_7$–Nb–C$_8$	101.3(2)	C6–Nb–P	121.1(11)
C7–Nb–P	76.88(11)	C8–Nb–P	76.19(11)

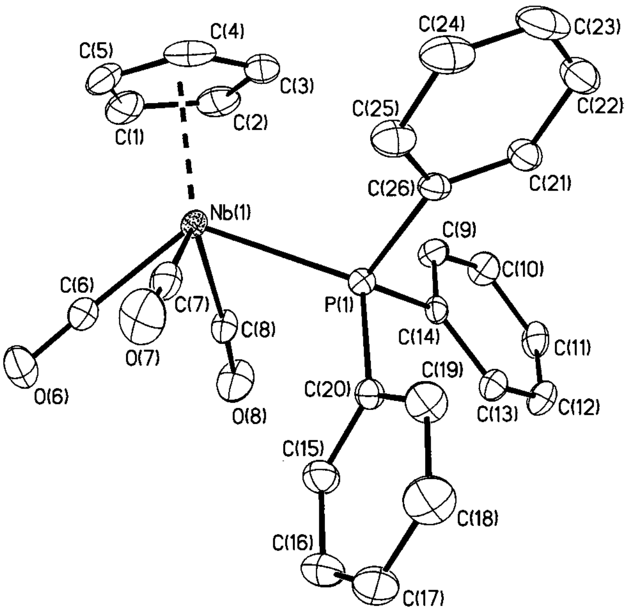


Fig. 4. Molecular structure of $(\eta^5\text{-}C_5H_5)Nb(CO)_3[P(C_6H_5)_3]$.

small size of vanadium and hence crowding of an associative intermediate.

Casey and his coworkers [10] have reported the reaction of $CpRe(CO)_3$ and $IndRe(CO)_3$ with phosphines to give η^1-C_5H_5 and η^1-C_8H_7 derivatives. It is presumed that these compounds pass though an η^3 intermediate. Similarly, Merola et al. [11] have isolated $(\eta^3\text{-}C_8H_7)Ir(CO)_2(PMe_3)$. In our studies we do not see any evidence for stabilized η^3 of η^1 intermediates for either $IndNb(CO)_4$ or $IndTa(CO)_4$, possibly because of the size of the ligands that were used and because the crowding of the $(\eta^3\text{-Ind})M(CO)_4L$ intermediates might strongly favor CO loss. It is possible that such intermediates might be stable with sterically undemanding ligands such as isocyanide.

Acknowledgements

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