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Ligand exchange processes of $OsHCl(CO)(L)(PR_3)_2$ (L = vacant, H_2, R′CN, O_2; R = Cy, *i*-Pr)

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Abstract

The reactivity of complexes formed by the addition of O_2, H_2 and R′CN to $OsHCl(CO)(PR_3)_2$ (**1a**:R = Cy; **1b**:R = *i*-Pr) has been examined. Under 24 bar H_2 and 65°C, the dioxygen ligand of $OsHCl(CO)(O_2)(PR_3)_2$ (**2a**,**b**) is displaced to yield the *trans*-hydridodihydrogen complexes $OsHCl(\eta^2\text{-}H_2)(CO)(PR_3)_2$ (**3a**,**b**). Measurements of the equilibrium constant, $K_{H_2} = [\mathbf{3a}]/[\mathbf{1a}][H_2]$, for the direct addition of H_2 to **1a** yield $\Delta H^\circ = -49.1 \pm 2.4$ kJ/mol and $\Delta S^\circ = -95.7 \pm 7.9$ J/mol K. **1a**,**b** react reversibly with aryl and alkyl nitriles to produce the isolable complexes, $OsHCl(CO)(R'CN)(PR_3)_2$ (**4a**,**b**). The phosphine ligands of **1a**,**b** and **3a**,**b** exchange with unbound, bulky alkyl phosphines at a rate that is slow relative to the NMR timescale. In the presence of excess PCy_3, complex **3b** yields the exchange products $OsHCl(\eta^2\text{-}H_2)(CO)(P\textit{i}\text{-}Pr_3)(PCy_3)$ and **3a**. While a tris-phosphine complex cannot be detected, limited kinetic data characterize the exchange as associative process.

Keywords: Osmium; Hydrogenation; High pressure NMR; Polymer modification; HNBR

1. Introduction

While the catalytic potential of mononuclear osmium complexes may have been overlooked in the past, new research has demonstrated their ability to facilitate a variety of reactions [1]. These include the hydrosilylation [2] of alkynes as well as the hydrogenation of alkenes and dienes through the activation of molecular hydrogen [3–8] or by hydrogen transfer [9,10]. We have recently discovered the exceptional efficiency with which complexes of the form $OsHCl(CO)(L)(PR_3)_2$ (**1**: L = vacant; **2**: L = O_2; **a**: R = Cy; **b**: R = *i*-Pr) catalyze the selective hydrogenation of acrylonitrile-butadiene copolymers [11]. Remarkably, these complexes are more active at industrial conditions than the current generation of Ru, Rh and Pd systems [12]. Nevertheless, this class of hydrogenation catalysts have received limited attention, especially at the more severe conditions employed in

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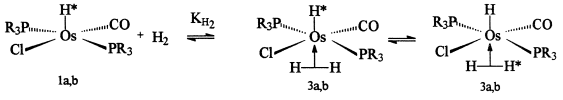
the HNBR industry ($P > 20$ bar, $T > 100$°C) [13].

Owing to their coordinative unsaturation, **1a**,**b** readily add small Lewis bases to form stable, six coordinate complexes. Moers [14], Moers and Langhout [15], and Moers et al. [16,17] have demonstrated the coordinative capacity of pyridine, SO_2, CS_2 and CO to **1a**. In addition to the CO analogue of **1b**, Esteruelas and Werner [18] have characterized the products of PMe_3 and $P(OMe)_3$ addition. It is also known that O_2 adds to **1a**,**b** to form the corresponding dioxygen adducts **2a**,**b** [19,5], which possess superior stability as solids. While unactivated olefins such as ethylene coordinate only weakly [19], electron withdrawing substituents ($CH_2=CHR$; R = –CN, $-CO_2Me$ or –COR) stabilize the Os–olefin bond sufficiently to yield isolable octahedral complexes [18,20].

Complex **1b** forms a dihydrogen complex (**3b**) through the η^2-coordination of H_2 [5,21,22]. Consistent with the addition reactions described above, dihydrogen coordinates *trans* to the hydride to create the Os(II) complex (Scheme 1). Since the removal of an H_2 atmosphere rapidly transforms **3b** into its five-coordinate precursor, this complex has yet to be isolated. However, the structure and dynamics of **3b** in solution have been studied in detail by Bakhmutov et al. [21] using NMR. In addition to a rapid exchange of free and bound H_2, **3b** undergoes fast hydrido-dihydrogen ligand exchange relative to the NMR timescale at temperatures greater than 10°C.

At present, our understanding of the reactions that constitute an acrylonitrile–butadiene copolymer hydrogenation remains incomplete, particularly at high pressures and temperatures. Outstanding issues include the fate of the dioxygen adducts **2a**,**b** when used as catalyst precursors as well as the propensity of nitrile to coordinate with **1a**,**b**. Furthermore, the PCy_3 analogue of **3b** remains uncharacterized in spite of its superior catalytic activity. In this short paper we present high-pressure ^{31}P and ^1H NMR data that furthers our knowledge of these matters. Preliminary studies of the lability of phosphine ligands within the **3a**,**b** system have helped to clarify their role in the hydrogenation process.



Scheme 1.

2. Experimental

Manipulation of solvents, reagents and samples was carried out with rigorous exclusion of air using either a Vacuum Atmospheres dry box or standard Schlenk techniques. H_2 (99.9% pure, < 1 ppm O_2) from Linde-Union Carbide, purified monochlorobenzene and toluene from Fischer Chemicals and deuterated solvents from Cambridge Isotopes were used as received. Benzonitrile, PCy_3, P*i*-Pr_3, PCp_3 and P*t*-Bu_3 from Strem Chemicals were used without further purification. Fully saturated acrylonitrile–butadiene copolymer was prepared by hydrogenating Krynac 38.50 from Bayer (38% acrylonitrile, $M_n = 70{,}000$, polydispersity = 3.6) using **2a** as a catalyst.

Variable-temperature NMR spectra were recorded on a Bruker AC-200 NMR spectrometer operating at 80.9 MHz and 200.1 MHz for ^{31}P and ^1H, respectively. ^1H chemical shifts were referenced to TMS using the residual methyl protons of toluene-d^8 or the aromatic resonance of benzene-d^6. ^{31}P signals were referenced using 85% H_3PO_4 as an external standard. Temperatures above ambient were calibrated against an 80% solution of ethylene glycol in DMSO while those below 25°C were measured using a 4% solution of methanol in CD_3OD. High-pressure spectra were recorded using a prototype of the apparatus developed by Roe [23]. This unit, consisting of a 5 mm sap-

phire tube epoxied to a titanium valve assembly, was inserted directly into a standard NMR probe.

2.1. Preparation of known compounds and complexes

To synthesize PMe*t*-Bu_2, a slight excess of BuLi in hexane was added dropwise to a THF solution of PH*t*-Bu_2 at 0°C. CH_3I in THF was then added slowly to generate the product in good yield. This THF solution of PMe*t*-Bu_2 was washed with water, decanted and dried with $MgSO_4$ before removing the solvent by distillation.

Complexes **1a** and **1b** were prepared by refluxing $OsCl_3 \cdot 3H_2O$ (Strem Chemicals) with the required phosphine in methoxyethanol and ethanol, respectively, and isolated by the procedure of Esteruelas and Werner [18]. Found for **1a**: ^{1}H NMR (C_6D_6): δ −32.6 (br. t); $^{31}P\{^1H\}$ NMR: (C_6D_6): δ 36.7 (s); IR (C_6H_6): ν(CO) 1886 cm^{-1}. Found for **1b**: ^{1}H NMR (C_6D_6): δ −30.4 (br. t); $^{31}P\{^1H\}$ NMR: (C_6D_6): δ 48.0 (s); IR (C_6H_6): ν(CO) 1889 cm^{-1}.

Complexes **2a** and **2b** were prepared by exposing hexane suspensions of **1a** and **1b**, respectively, to pure O_2 as detailed by Esteruelas et al. [7]. Found for **2a**: ^{1}H NMR (C_6D_6): δ −2.5 (t), $^2J_{P-H} = 30.4$ Hz; $^{31}P\{^1H\}$ NMR: (C_6D_6): δ 13.7 (s); IR (nujol): ν(CO) 1948 cm^{-1}. Found for **2b**: ^{1}H NMR (C_6D_6): δ −2.43 (t), $^2J_{P-H} = 30.1$ Hz; $^{31}P\{^1H\}$ NMR: (C_6D_6): δ 23.4 (s); IR (nujol): ν(CO) 1945 cm^{-1}.

2.2. Preparation of $OsHCl(CO)(PhCN)(PR_3)_2$ (**4a**: R = Cy; **4b**: R = i-Pr)

A suspension of ca. 0.3 g **1a** or **1b** in 5 ml hexane was treated with an excess (ca. 0.2 ml) of PhCN at 23°C. The mixture was stirred for 10 min, resulting in a colour change from brown to yellow. The solution was decanted and the solid washed with MeOH (2 × 5 ml) and diethyl ether (1 × 5 ml) and dried under vacuum. Found for **4a**: ^{1}H NMR (C_6D_6): δ −12.3 (t), $^2J_{P-H}$ = 19.0 Hz; $^{31}P\{^1H\}$ NMR: (C_6D_6): δ 14.5 (s); IR (C_6H_6): ν(CO) 1883 cm^{-1}, ν(CN) 2230 cm^{-1}. Found for **4b**: ^{1}H NMR (C_6D_6): δ −12.6 (t), $^2J_{P-H} = 18.5$ Hz; $^{31}P\{^1H\}$ NMR: (C_6D_6): δ 24.1 (s); IR (C_6H_6): ν(CO) 1885 cm^{-1}, ν(CN) 2232 cm^{-1}.

2.3. Measurement of equilibrium constants, K_{H_2} and K_{CN}

The methodology used to measure K_{H_2} for the **1a**–**3a** equilibrium was developed by Bakhmutov et al. [21]. To similarly characterize the **1a**–**4a** equilibrium, a ^{31}P NMR variation of the technique was employed. A monochlorobenzene solution containing 0.0127 M of **1a** and 0.0119 M of R′CN from hydrogenated acrylonitrile–butadiene copolymer was charged to a sapphire NMR tube and sealed under N_2. The ratio, $X = [\mathbf{4a}]/[\mathbf{1a}]$was determined from the chemical shift of the exchanged averaged phosphine resonance according to:

$$X = \frac{[\mathbf{4a}]}{[\mathbf{1a}]} = \frac{\delta(\text{avg}) - \delta(\mathbf{1a})}{\delta(\mathbf{4a}) - \delta(\text{avg})}.$$

Material balances on the total osmium and nitrile charged to the system yield:

$$[\text{Os}]_T = [\mathbf{1a}] + [\mathbf{4a}]$$

$$[\text{R}'\text{CN}]_T = [\mathbf{4a}] + [\text{R}'\text{CN}].$$

It follows that the equilibrium constant K_{CN} may be expressed as:

$$K_{CN} = \frac{X}{[\text{R}'\text{CN}]_T - X/(1+X)[\text{Os}]_T}.$$

δ(**1a**) and δ(**4a**) were measured at 23, 70, 110, 132°C using a solution of pure **1a** and one containing **1a** plus 60 equivalents of nitrile, respectively. Interpolation of these data provided the estimates of δ(**1a**) and δ(**4a**) required to calculate K_{CN} at each temperature.

The formation constants $\Delta H°$ and $\Delta S°$ for the **1a**–**3a** and the **1a**–**4a** equilibria were calculated from a non-linear, least-squares regression of

$$K = \frac{\Delta S°}{R}\exp\left(-\frac{\Delta H°}{RT}\right).$$

Estimates of $\Delta H°$ and $\Delta S°$ are accompanied by 95% confidence intervals.

2.4. Measurement of phosphine exchange rates

To a known mass of **1b** was added a solution of the required phosphine in toluene-d^8. Once charged to the sapphire NMR tube, the N_2 atmosphere was purged with hydrogen and an H_2 pressure of 24 bar was applied. At 23°C, no phosphine exchange could be detected during this sample preparation. Therefore, time zero was marked by the insertion of the sample into the preheated NMR probe. The concentrations of exchange products were measured at 2-h intervals by $^{31}P\{^1H\}$ NMR using an inverse-gated pulse sequence. Estimates of k_1 and k_{-1} were derived from a least-squares regression of $d[\mathbf{3b}]/dt$ vs. product concentrations as per Eq. (1) of the text.

3. Results and discussion

3.1. Fate of *2a,b* exposed to hydrogenation conditions

At ambient temperature, O_2 will displace olefin or H_2 from $OsHCl(CO)(L)(PR_3)_2$ to produce the dioxygen adducts **2a**,**b** [19,5]. The air stability of these solids makes them convenient catalyst precursors, and **2b** has been used as such for the hydrogenation of phenylacetylene [3]. In this application, an observed induction period was attributed to the displacement of O_2 by the alkyne. We have observed that refluxing **2a** with excess PCy_3 in methoxyethanol regenerates **1a** in good yields, indicating that while it may be strongly bound, O_2 can be dissociated to yield a five coordinate complex.

Fig. 1 illustrates the response of **2b** when exposed to hydrogenation conditions that approach those applied industrially. Under N_2 at 23°C, the $^{31}P\{^1H\}$ NMR spectrum of **2b** consists of a singlet at 23.4 ppm. Exposed to 24 bar H_2 at 65°C, the **2b** signal is quickly replaced by the singlet at 36.1 ppm that is characteristic of **3b**. This transformation of **2b** to **3b** is confirmed in the ^1H NMR spectrum and has been observed

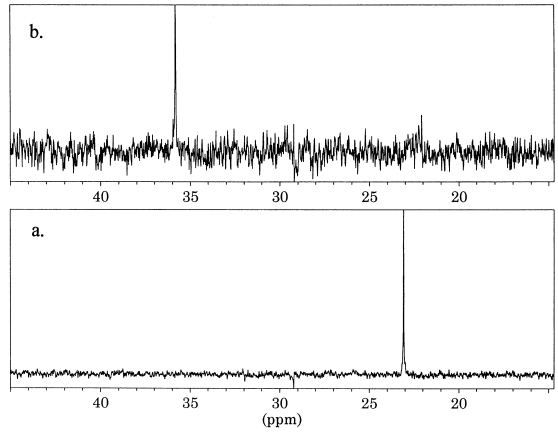


Fig. 1. $^{31}P\{^1H\}$ NMR spectra illustrating the transformation of **2b** to **3b**; $P_{H_2} = 24$ bar, $T = 65$°C. (a) Complex **2b** at 25°C, 1 atm N_2. (b) Complex **2b** at 65°C, 24 bar H_2 after 1 min.

for the PCy_3 analogues. Consequently, the catalytic behaviour of **2a**,**b** is expected to be identical to that observed for the five-coordinate complexes, **1a**,**b**.

Over the time frame of minutes, a colour change from pale yellow to deep violet is accompanied by the degradation of the NMR signal. While detectable levels of phosphine oxide can be observed, the structure and composition of the resulting osmium complex are unknown. The instability of these dioxygen adducts in solution is consistent with the observations of Mezzeti et al. [24] for $[OsCl(O_2)(dcpe)_2][BPh_4]$. However, the effect of dissociated O_2 on industrial hydrogenations is likely to be negligible, due to the insignificant concentration of O_2 created by catalytic amounts of **2a**,**b** when charged to a high H_2 pressure environment.

3.2. Thermodynamics of H_2 addition to *1a*

Complex **1a** reacts with H_2 to produce a *trans*-hydrido-dihydrogen complex, $OsHCl(CO)(\eta^2\text{-}H_2)(PCy_3)_2$ (**3a**). This complex is the PCy_3 analogue of the P*i*-Pr_3 system previously synthesized by Esteruelas et al. [7]. The interactions of H_2 with **1b** have been studied in detail by Bakhmutov et al. [21] in terms of the rate of H_2 exchange and the equilibrium distribution of

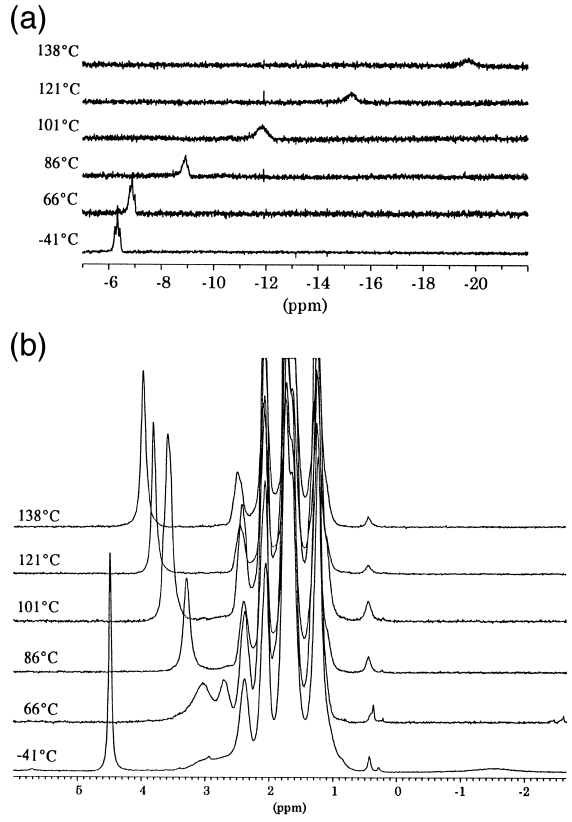
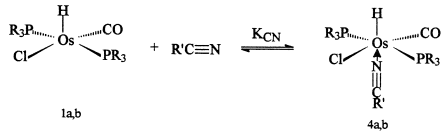


Fig. 2. ^{1}H NMR spectra of the **1a**–**3a** system under rapid exchange; (a) Hydride region, (b) Os(η^2-H_2)/free H_2 region.

products (Scheme 1). Having identified the corresponding exchange process for the PCy_3 system, we have adopted their experimental



Scheme 2.

methodology to similarly characterize the **1a**–**3a** equilibrium.

The relative abundance of **1a** and **3a** was determined by ^{1}H NMR from the exchange averaged chemical shift of the hydride resonance (Fig. 2a) while the distribution of free and coordinated H_2 was measured from the position of the exchange averaged dihydrogen resonance (Fig. 2b). The equilibrium constants ($K_{H_2} = [\mathbf{3a}]/[\mathbf{1a}][H_2]$) calculated from these spectra are listed in Table 1. Least squares regression of the response of K_{H_2} to changes in temperature yields $\Delta H^\circ = -49.1 \pm 2.4$ kJ/mol and $\Delta S^\circ = -95.7 \pm 7.9$ J/mol · K. These compare with reported values of $\Delta H^\circ = -59.0 \pm 2.1$ kJ/mol and $\Delta S^\circ = -125.0 \pm 4.2$ J/mol · K for the **1b**–**3b** equilibrium [21].

3.3. Reactivity of *1a,b* with nitriles

The deleterious influence of nitrile on hydrogenation activity has been reported for a number of efficient catalyst systems. Mohammadi and Rempel [25] have observed the inhibition of

Table 1
^{1}H NMR study of the **1a**–**3a** equilibrium; K_{H_2} vs. temperature

Temperature (K)	δ_{avg} H_2 (ppm dihydrogen region)	δ_{avg} Os–H (ppm hydride region)	K_{H_2} (M^{-1})
307	3.04	−6.85	2345
340	3.33	−8.85	375
360	3.63	−11.80	122
374	3.86	−15.35	51.5
394	4.02	−19.55	25.6
411	4.12	−23.80	15.1

$[Os]_T = 6.68 \times 10^{-3}$ M.
δ_{H_2}(free) = 4.50 ppm.
δ_{H_2}(bound) = −1.52 ppm.
$\delta_{\mathbf{1a}} = -32.65$ ppm.
$\delta_{\mathbf{3a}} = -6.31$ ppm.

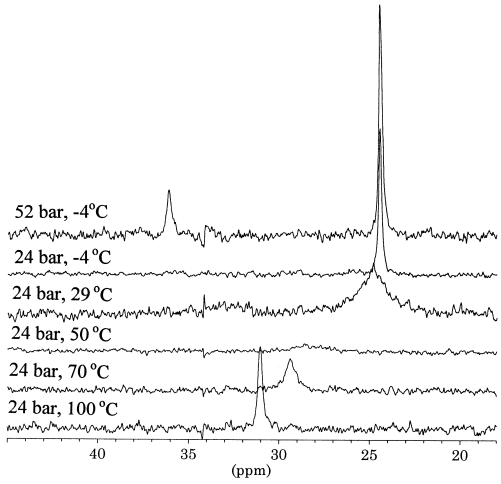


Fig. 3. Variable temperature $^{31}P\{^1H\}$ NMR study of the **3b**–**4b** equilibrium; 1.25 equiv. PhCN.

$RhCl(PPh_3)_3$ by the nitrile within NBR as have Martin et al. [26] for the $RuHCl(CO)(PCy_3)_2$ system. In a study of $OsH_2(dcpe)_2$, Farneti et al. [27] attributed the relatively low rate of PhHC=CH–CN hydrogenation to a competitive coordination of nitrile to the metal centre. We have recently demonstrated a similar influence of nitrile on the activity of **2a** [12]. To establish the mode and significance of nitrile coordination, we have isolated and characterized alkyl and aryl nitrile complexes of **1a**,**b**.

Solutions of **1a**,**b** rapidly transform from brown to yellow with the addition of one equivalent of PhCN. A sharp new singlet appears in the ^{31}P NMR spectra at 14.5 ppm for **4a** and 24.1 ppm for **4b**. The hydride resonance in the ^1H NMR spectrum shifts downfield (**4a**: −12.3 ppm; **4b**: −12.6 ppm) suggesting that nitrile is *trans* disposed (Scheme 2) as is the case with other addition reactions of this system. Precedents for nitrile complexes of this type are abundant. Gilbert and Wilkinson [28] have prepared $RuCl_2(PhCN)(PPh_3)_3$ by heating under reflux $RuCl_2(PPh_3)_3$ with benzonitrile. A recent report by Schlaf et al. [29] has defined the reactivity of the osmium–nitrile complex $[Os(\eta^2\text{-}H_2)(MeCN)(dcpe)_2][BPh_4]_2$. In both of these cases, σ-donation of the nitrogen lone pair is the accepted mode of nitrile coordination.

The relative stabilities of the nitrile and H_2 complexes of **1** are demonstrated by $^{31}P\{^1H\}$ NMR spectra of **1b** containing 1.25 equivalents of PhCN (Fig. 3). At −4°C and 53 bar H_2, two singlets corresponding to **3b** and **4b** are resolved. Considering the intensity of the signals, the coordination of nitrile is favoured at this temperature. Reducing the system pressure by half produces the expected shift of the equilibrium towards the nitrile complex. Warming the sample to 29°C produces two exchange broadened signals, one at 32.5 ppm and a more pronounced resonance at 24.5 ppm. These coalesce at 50°C as the system reaches the fast exchange limit of the NMR timescale. At 70°C and beyond, the chemical shift of the exchanged averaged **3b** ↔ **4b** signal is evidence of an equitable distribution of the two complexes, in spite of the higher concentration of H_2 relative to R′CN. This suggests that during the hydrogenation of a nitrile copolymer, complexes **3** and **4** are the predominant chemical species.

Table 2
$^{31}P\{^1H\}$ NMR study of the **1a**–**4a** equilibrium. Hydrogenated acrylonitrile–butadiene copolymer in monochlorobenzene

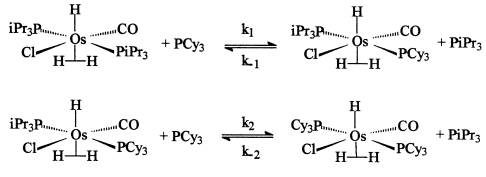
Temperature (K)	$\delta_{\mathbf{1a}}$ (ppm)	$\delta_{\mathbf{4a}}$ * (ppm)	Temperature (K)	δ^{+}_{avg} (ppm)	$X = [\mathbf{4a}]/[\mathbf{1a}]$	K_{CN} (M^{-1})
296	37.17	13.86	351	18.50	4.595	3050
323	37.37	–	367	21.04	2.560	914
343	37.55	14.28	388	25.84	1.085	204
383	37.78	14.68	406	29.76	0.503	65.6
405	37.95	15.03				

*[**1a**] = 0.0161 M; [R′CN] = 0.6450 M.
+[**1a**] = 0.0127 M; [R′CN] = 0.0119 M.

In the fast exchange domain ($T > 70$°C) the ^{31}P chemical shift of the exchanged averaged **1a** ↔ **4a** resonance reflects the relative abundance of these complexes in solution. We have exploited this principle to derive the equilibrium constant, $K_{CN} = [\mathbf{4a}]/[\mathbf{1a}][R'CN]$, for the addition of the alkyl nitrile found in hydrogenated acrylonitrile–butadiene copolymer to **1a**. The chemical shifts of complexes **1a** and **4a** and the exchange averaged **1a** ↔ **4a** resonance are listed in Table 2 along with the calculated equilibrium constants. The influence of temperature on K_{CN} yields, for the formation of **4a** from **1a** and hydrogenated acrylonitrile–butadiene copolymer, $\Delta H^\circ = -81.2 \pm 2.8$ kJ/mol and $\Delta S^\circ = -165 \pm 7.3$ J/mol · K.

3.4. Phosphine exchange processes of *3b*

The results of our catalytic research have shown that one equivalent of PCy_3 relative to [**2a**] reduced the hydrogenation activity by an order of magnitude [12]. While central to the hydrogenation mechanism, this result is difficult to rationalise. One possibility is the coordination of a third phosphine to the coordinatively unsaturated complex, **1a**. While the PPh_3 analogue of **1a** is the tris-phosphine complex, $OsHCl(CO)(PPh_3)_3$ [30], all attempts by Moers [14] to prepare $OsHCl(CO)(PCy_3)_3$ were unsuccessful. Esteruelas and Werner [18] have isolated products of PMe_3 and $P(OMe)_3$ addition to **1b**, but observed no similar coordination of a third P*i*-Pr_3 ligand. Consistent with these reports, we observed no change in the room temperature ^{31}P NMR spectra of **1a** or **1b** when exposed to an excess of their respective phosphines.



Scheme 3.

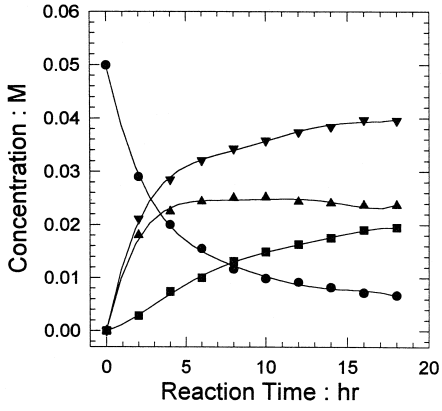


Fig. 4. Exchange product concentrations vs. time; $P_{H_2} = 24$ bar, $T = 71$°C, $[PCy_3]_0 = 0.32$ M. ● $Os(P\textit{i}\text{-}Pr_3)_2$, ■ $Os(PCy_3)_2$, ▲ $Os(P\textit{i}\text{-}Pr_3)(PCy_3)$, ▼ P*i*-$Pr_3$; Os = $OsHCl(CO)(H_2)$.

The influence of phosphine on the hydrogenation activity of **2a** could also result from an unfavourable shift of a required PCy_3 dissociation equilibrium. However, ^{31}P spectra of **1a**,**b** recorded in toluene at 100°C under N_2 or H_2 showed no sign of dissociated phosphine. While it therefore appears that direct evidence to support either inhibition mechanism is unavailable, the phosphine ligands bound to **1a**,**b** and **3a**,**b** are labile. We have observed that charging a second bulky, alkyl phosphine to a solution of **1** or **3** yields a mixture of the original complex, the monosubstituted complex and the disubsti-

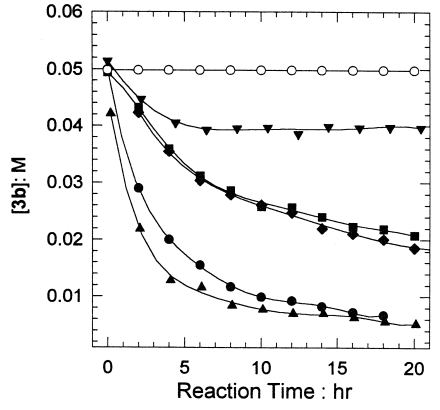


Fig. 5. [**3b**] vs. time for different phosphines; $P_{H_2} = 24$ bar, $T = 71$°C. ○ $[PtBu_3]_0 = 0.13$ M, ▼ $[PMet\text{-}Bu_2]_o = 0.13$ M, ■ $[PCy_3]_0 = 0.11$ M, ◆ $[PCy_3]_0 = 0.10$ M, ● $[PCy_3]_0 = 0.32$ M, ▲ $[PCp_3]_0 = 0.11$ M.

Table 3
Phosphine exchange rate constants

Phosphine	$[PR_3]$ M	k_1 $(M\,h)^{-1}$	Lower⟨95%⟩Upper		k_{-1} $(M\,h)^{-1}$	Lower⟨95%⟩Upper	
PCy_3	0.10	0.814	0.729	0.899	0.461	0.148	0.773
PCy_3	0.11	0.873	0.802	0.945	0.914	0.358	1.469
PCy_3	0.32	0.842	0.762	0.922	0.531	−0.055	1.117
P*Me*-Bu_2	0.13	0.773	0.677	0.870	17.04	12.98	21.10
P*t*-Bu_3	0.13	0.000	–	–	–	–	–
PCp_3	0.11	2.72	2.48	2.96	0.714	0.113	1.314

$P_{H_2} = 24$ bar.
$T = 71$°C.

tuted product. Scheme 3 illustrates this process for the **3b** + PCy_3 system. Both substitution reactions are reversible, and the product distributions can be established from charging PCy_3 to **3b** or by adding P*i*-Pr_3 to a solution of **3a**.

Up to 130°C, the rate of exchange between free P*i*-Pr_3 and that bound to **3b** is insufficient to support spin-saturation labelling as a kinetic method. Therefore, a traditional study was undertaken wherein the concentration of the exchange products was monitored with time by ^{31}P NMR. All the data acquired in one of the **3b**–PCy_3 exchange experiments are presented in Fig. 4. Plots of [**3b**] vs. time illustrate the key result of each experiment (Fig. 5). The reproducibility of the experimental technique is evident from the two trials employing $[PCy_3] = 0.1$ M (Fig. 5).

To quantify the first substitution reaction in which **3b** is transformed into OsHCl(CO)-(H_2)(P*i*-Pr_3)(PR_3), the rate constants k_1 and k_{-1} defined by Scheme 3 have been fitted to the second-order rate expression:

$$-\frac{d[\mathbf{3b}]}{dt} = k_1[\mathbf{3b}][PR_3] - k_{-1}[\mathrm{OsHCl(CO)} \times (H_2)(P\textit{i}\text{-}Pr_3)(PR_3)][P\textit{i}\text{-}Pr_3] \quad (1)$$

An estimate of k_1 represents the inherent rate of the forward substitution reaction at a given phosphine type and concentration. Regression values of k_1 and k_{-1} are listed in Table 3. The three PCy_3 trials yield a single set of rate constants, as would be expected if Eq. (1) was a suitable model for the process.

From this limited set of data, the exchange rate appears to depend on the nature and abundance of the entering phosphine, which is evidence of an associative-type mechanism. That P*t*-Bu_3 does not participate in such an exchange process is not surprising, given its extraordinary cone angle of 180°. Nevertheless, an unequivocal assignment of an exchange mechanism based on such few data is unwarranted.

4. Conclusions

When employed as a hydrogenation catalyst precursor, **2** is activated by O_2 displacement by H_2 to form the dihydrogen complex, **3**. However, solutions of **2** will decompose over time unless dissociated O_2 is expelled from solution. During the hydrogenation of acrylonitrile–butadiene copolymers, the predominant complexes are the nitrile and H_2 adducts, **4** and **3**, respectively. Under typical hydrogenation conditions, the coordination of R′CN to **1** can account for a reduction in catalytic activity associated with increased copolymer concentration. The phosphine ligands of **1** and **3** are labile, undergoing exchange with free PR_3 at a rate that is slow relative to the NMR timescale. Preliminary kinetic data suggests this is an associative process.

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