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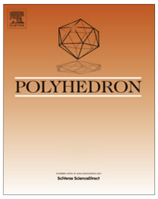

Hexamethylphosphorus triamide: A chloride-for-dimethylamido, Me_2N^-, exchange reagent

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Dedicated to the memory of Michelle Millar, whose warmth and sense of humor are missed.

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ABSTRACT

The reaction of $P(NMe_2)_3$ with WCl_6 produces $[ClP(NMe_2)_3][WCl_4(NMe_2)_2]$, $[ClP(NMe_2)_3][2]$, through apparent Cl^--for-NMe_2^- exchange. A six-coordinate $[Cl_5W–PCl(NMe_2)_3]$ metallophosphorane species is proposed as a probable intermediate in this ligand exchange reaction. A similar reaction with $NbCl_5$ results in a more complex product, $[NbCl_4(NHMe_2)(\eta^2\text{-}N(Me)–C(H)–P(NMe_2)_3)]$, **3**, in which Cl^--for-NMe_2^- exchange is attended by additional reactions that include C–H activation and cyclometallation of an NMe_2^- ligand, H^+ transfer to NMe_2^- to form a dimethylamine ligand, and adduct formation between exogenous $P(NMe_2)_3$ and the formyliminium carbon resulting from cyclometallation. Structural characterization of $[ClP(NMe_2)_3][2]$ reveals a *cis* disposition of NMe_2^- ligands that are oriented at 63.2° relative to one another and an appreciable lengthening of the W–Cl bonds *trans* to the NMe_2^- ligands (2.4615[4] Å) as compared to those that are *cis* (2.3918[4] Å). The structure of **3** is distorted pentagonal bipyramidal with the formyliminium carbon and nitrogen atoms arranged slightly above and below by ~0.37 Å the equatorial plane. The potential synthetic utility of $P(NMe_2)_3$ as an alternative to the classical method of delivery of dialkylamido ligands via $LiNR_2$ is discussed.

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1. Introduction

Dialkyl amido anions are widely employed as supporting ligands in transition metal coordination chemistry because they enjoy high basicity both as σ and π-donors [1], ready access either commercially or synthetically, and amenability to the incorporation of solubilizing or sterically encumbering groups on the nitrogen atom [2]. The typical method by which dialkylamido ligands are delivered to a transition metal center is via metathesis of chloride ligand using an alkali metal salt of the amido anion [3–10].

In the course of some efforts aimed at synthesis of tungsten complexes with $P(NMe_2)_3$ as a supporting ligand, we observed a limited tendency of this phosphine to effect Cl^--for-NMe_2^- exchange at the tungsten center [11]. These ligand substitutions appeared to be restricted to one or two occurrences in a given compound even though the possibility existed for additional exchanges. These observations, described here in greater detail, lead us to suggest the potential utility of $P(NMe_2)_3$ as a mild and selective reagent for the delivery of one or two NMe_2^- ligands to high-valent early or middle transition metal complexes.

2. Experimental

2.1. General considerations

All glassware was oven-dried, and all reactions and manipulations were conducted using standard Schlenk techniques or glove boxes. Prior to their use, toluene, *n*-pentane, and CH_2Cl_2 were dried by passage through a system of drying columns from the Glass Contour Company. The numbering system defined in Fig. 1 is used to identify the compounds in the following discussion.

2.2. Physical methods

Electrochemical measurements were made with a CHI620C electroanalyzer workstation using a Ag wire reference electrode, a platinum disk working electrode, Pt wire as auxiliary electrode, and $[Bu_4N][PF_6]$ as the supporting electrolyte. The $[Cp_2Fe]^+/Cp_2Fe$ couple occurred at +0.49 mV (by CV) in 0.10 M $[Bu_4N][PF_6]$ in THF. The UV–vis spectrum (molar absorptivities reported in M^{-1} - cm^{-1}) was obtained at ambient temperature with a Hewlett–Packard 8452A diode array spectrometer, and the elemental analysis was performed by Midwest Microlab, LLC of Indianapolis, IN. Details regarding growth of crystals, collection and processing of X-ray diffraction data, and the solution and refinement of all crystal structures are deferred to Supplementary data. Final unit cell and

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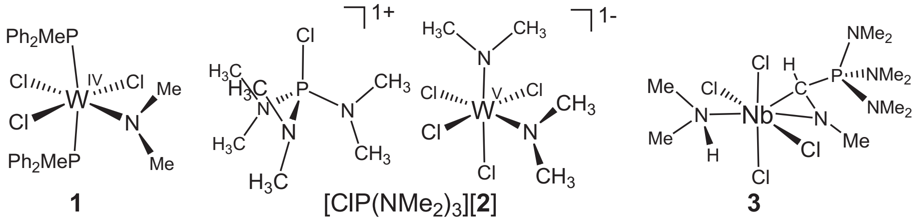

Fig. 1. Metal complexes resulting from Cl^--for-NMe_2^- exchange with $P(NMe_2)_3$.

refinement data for both crystal structures are presented in Table 1.

2.3. Preparation of [ClP(NMe$_2$)$_3$][WCl$_4$(NMe$_2$)$_2$], [ClP(NMe$_2$)$_3$][2]

A 200 mL Schlenk flask was charged with WCl_6 (0.723 g, 1.82 mmol) and 50 mL of dry toluene. To this mixture was added $P(NMe_2)_3$ (0.975 mL, 5.36 mmol) in 10 mL of toluene. Upon addition, a purple color developed, and stirring was continued for an hour, during which time the color of the solution turned to reddish orange. A reflux condenser was connected to the flask, and the mixture was refluxed for an additional hour. Once the solution cooled to room temperature, the solvent was reduced to ~20 mL and allowed to stand overnight without stirring. Reddish colored plate-like crystals deposited at the bottom of the flask. The flask was cooled at −20 °C for 12 h; crystals were collected by filtration and dried *in vacuo*. Yield: 0.358 g, 32%. The $[W^VCl_4(NMe_2)_2]^{1-}$ anion was not observable by ^1H NMR owing to its paramagnetism. Absorption spectrum (CH_2Cl_2), λ_{max} in nm (ε_M): 376 (1900), ~488 (sh, 520). Cyclic voltammetry (THF): $W^V \rightarrow W^{VI} + e^-$, 0.841 V. *Anal.* Calc. for $C_{10}H_{30}Cl_5N_5PW$: C, 19.61; H, 4.94; N, 11.43. Found: C, 19.58; H, 4.91; N, 11.42.

2.4. Preparation of [NbCl$_4$(NMe$_2$H)(((formyl-N-methyl)iminium-κN)-1-tris(dimethylamino)-phosphane)- κC^1], 3

A 200 mL Schlenk flask was charged with a stir bar, $NbCl_5$ (0.196 g, 0.72 mmol) and 30 mL of dry toluene, while $P(NMe_2)_3$ (0.196 mL, 1.08 mmol) in 5 mL toluene was separately added to a 50 mL Schlenk flask. The phosphine solution was transferred via cannula to the $NbCl_5$ mixture in toluene, which induced an immediate color change from yellow to reddish-orange. A reflux condenser was attached to the reaction vessel, and the solution was refluxed under N_2 for 3 h. After cooling to ambient temperature, the solvent was evaporated under reduced pressure, and a waxy solid was obtained. This solid was washed with pentane and dried under vacuum. Crystalline product was obtained the diffusion of *n*-pentane vapor into a concentrated CH_2Cl_2 solution. ^1H NMR (δ, ppm in C_6D_6): 2.38 (d, *J* = 12.0 Hz, 18H, $P(N(CH_3)_2)_3$), 2.48 (d, *J* = 8.5 Hz, 6H, $NH(CH_3)_2$), 2.64 (d, *J* = 9.9 Hz, 3H, $N(CH_3)$=CH), ~3.23 (br, 1H, $NH(CH_3)_2$), 4.38 (s, 1H, $N(CH_3)$=C*H*).

Table 1
Summary of Unit Cell and Refinement Data for [ClP(NMe$_2$)$_3$][2] and **3**.

Compound	[ClP(NMe$_2$)$_3$][2]	**3**
Solvent	none	none
Formula	$C_{10}H_{30}Cl_5N_5PW$	$C_{10}H_{29}Cl_4N_5NbP$
Formula weight	612.46	485.06
xtl system	orthorhombic	monoclinic
space grp	$P2_12_12_1$	$P2_1/n$
Color, habit	orange plate	red slat
a (Å)	8.5132(16)	8.5893(3)
b (Å)	10.3768(7)	18.0894(7)
c (Å)	25.0459(17)	13.1383(5)
α (°)	90	90
β (°)	90	90.231(1)
γ, (°)	90	90
V (Å^3)	2212.5(3)	2041.35(13)
T (K)	100	100
Z	4	4
R_1[a], wR_2[b]	0.0132, 0.0274	0.0434, 0.1159
Goodness-of-fit (GoF) on F2	1.030	1.043

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)$ for [ClP(NMe$_2$)$_3$][2]; $w = 1/[\sigma^2(F_o^2) + (0.618P)^2 + 4.4092P]$, where $P = (F_o^2 + 2F_c^2)/3$ for **3**.

3. Discussion

Treatment of *trans*-$[W^{IV}Cl_4(PMePh_2)_2]$ with two eq. of $P(NMe_2)_3$ in an attempt to effect phosphine substitution was observed to produce modest (~15%) but reproducible quantities of $[W^{IV}Cl_3(NMe_2)(PMePh_2)_2)]$, **1**, (Fig. 1). This synthetic foray was part of a study of the reduction potentials and reactivity of mid- and low-valent chlorophosphine tungsten complexes that are of interest for their small molecule reactivity [11]. In the context of this effort, $[WCl_6]$ was reacted with a several-fold excess of $P(NMe_2)_3$ with the expectation of forming *trans*-$[W^{IV}Cl_4(P(NMe_2)_3)_2]$ according to a published procedure for preparation of such complexes [12]. However, bulk crystallization, which could be accomplished more cleanly and in substantively better yield than for $[W^{IV}Cl_3(NMe_2)(PMePh_2)_2]$, led to the isolation of [ClP(NMe$_2$)$_3$][*cis*-$W^VCl_4(NMe_2)_2$], [ClP(NMe$_2$)$_3$][2], a product in which both reduction and ligand exchange at tungsten have occurred (Fig. 1). The methyl groups of the NMe_2 ligands in $[2]^{1-}$ were not observed by ^1H NMR owing to the compound's paramagetism.

The observation of both nonredox ligand exchange (in **1**) and of ligand exchange attended by reduction (in $[2]^{1-}$) suggests that the reduction and ligand exchange processes are not necessarily related and may occur as separate events. The transformation of $[WCl_4(PMePh_2)_2]$ to **1** likely begins with $P(NMe_2)_3$ association to afford the 7-coordinate complex shown as (**b**) in Scheme 1, examples of which have been identified structurally [13–14]. A plausible intermediate leading to **1** is a metallophosphorane species ((**d**) in Scheme 1) formed by internal transfer of chloride to the phosphorus atom of $P(NMe_2)_3$. The transition state (**c**) through which this metallophosphorane forms would have an analog (**e**) involving a dimethylamido group, thus providing for facile Cl^--for-NMe_2^- exchange between tungsten and phosphorus and ultimate dissociation of $PCl(NMe_2)_2$. Metallophosphorane species such as (**d**) have been implicated experimentally and assessed computationally in related types of exchange reactions with phosphine ligands [15–16]. It is noteworthy that halide-for-NR_2^- exchange does not appear to have been previously described.

A possible driving force for this P–NMe_2 bond scission and ligand exchange is enhanced stabilization of the W^{IV} center by the strong π-donating NMe_2^- ligand. The stabilization thus conferred upon the W^{IV} center appears to attenuate its reactivity such that further ligand exchange is suppressed. A report of facile formation of $PCl(NMe_2)_2$ from $P(NMe_2)_3$ and Me_3SiCl via a phosphonium

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