trend in $k_{-1}/k_2$ should thus be influenced solely by $k_2$, the second-order rate constant for the replacement of a solvent molecule in the intermediate by tertiary phosphine. The trend is the same as that observed previously for $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$ in acetonitrile and with $[(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2Cy]$ in dimethyl sulfoxide.[2] In keeping with the lower steric congestion in the manganese complex, the decrease in $k_2$ is less abrupt and reactivity extends to higher cone angles (e.g., tricyclohexylphosphine (170°) reacts with $[(CO)_5MnCH_2Ph]$ at 30 °C, but with neither of the cyclopentadienylmetal compounds).

**Registry No.** THF, 109-99-9; 2-MeTHF, 96-47-9; 2,5-$Me_2$THF, 1003-38-9; $[(CO)_5MnCH_2C_6H_5]$, 14049-86-6; $[(CO)_5MnCH_2C_6H_4$-*o*-Me], 95891-55-7; $[(CO)_5MnCH_2C_6H_4$-*p*-Me], 95891-56-8; $[(CO)_5MnCH_2C_6H_2$-2,4,6-$Me_3]$, 95891-57-9; $[(CO)_5MnCH_2C_6H_2$-2,4,6-(*i*-Pr)$_3]$, 95891-58-0; $[(CO)_5MnCH_2C_6Me_5]$, 56800-76-1; $Ph_3P$, 603-35-0; $PMe_2Ph$, 672-66-2; P-*n*-$Bu_3$, 998-40-3; $PMePh_2$, 1486-28-8; $PEtPh_2$, 607-01-2; P-*i*-$PrPh_2$, 6372-40-3; P-*t*-$BuPh_2$, 6002-34-2; $P(C_6H_{11})_3$, 2622-14-2; CO, 630-08-0.

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# Preparation and Chemistry of Novel Platinum(II) Amide Complexes Containing β-Hydrogens[†]

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*Summary:* Synthesis of new platinum(II) amide complexes has been accomplished both by metathesis of $L_2PtR(Cl)$ ($L_2$ = DPPE = 1,2-bis(diphenylphosphino)ethane, R = $CH_3$, $CH_3$, $C_6H_5$, $CH_2C_6H_5$; $L_2$ = DMPE = 1,2-bis(dimethylphosphino)ethane, R = $CH_3$), with $LiNCH_3(C_6H_5)$ and by exchange of free amine with the analogous methoxide complexes. (DPPE)$PtCH_3[N(CH_2C_6H_5)(H)]$, prepared from (DPPE)$PtCH_3(Cl)$ and $LiN(CH_2C_6H_5)(H)$, reacts with CO to give (DPPE)$PtCH_3[C(O)N(CH_2C_6H_5)(H)]$. (DMPE)$PtCH_3[NCH_3(C_6H_5)]$ crystallizes from THF/hexane in space group $P2_1/n$ with cell dimensions $a$ = 6.2790 (8) Å, $c$ = 16.894 (2) Å, and $\beta$ = 96.47 (1)° with $Z$ = 4. The favorable equilibrium for the displacement of methanol by *N*-methylaniline suggests the metal–nitrogen bond is much less prone to dissociation of amide than are metal–oxygen bonds to dissociation of methoxide and requires the Pt–$OCH_3$ homolytic bond strength be 16 kcal/mol stronger than the Pt–$NCH_3(C_6H_5)$ bond. Reaction of (DPPE)$PtCH_3(NCH_3(C_6H_5))$ with methyl iodide and acetyl chloride shows these amide complexes react as nucleophiles despite their inability to dissociate free amide.

Late-transition-metal amide complexes have been postulated in several amine based routes to organic nitrogen-containing chemicals.[1] For example, the reaction of amines with carbon monoxide and oxygen to give carbamates is a potential route to important insecticides; it may involve late metal amides[1a,b] and would, if successfully developed, preclude the need to prepare and handle dangerous isocyanates and phosgene. Despite this potential, very little is known about the chemistry of late-transition-metal amide complexes primarily because relatively few such compounds are known and those possessing β-hydrogen atoms are particularly difficult to isolate.[2] We wish to report the synthesis of Pt(II) alkyl amide complexes and several reactions that demonstrate the reactivity of the platinum–nitrogen bond.

Reaction of $L_2PtR(Cl)$ ($L_2$ = DPPE = 1,2-bis(diphenylphosphino)ethane, R = $CH_3$, $C_6H_5$, $CH_2C_6H_5$; $L_2$ = DMPE = 1,2-bis(dimethylphosphino)ethane, R = $CH_3$[3]) with 1 equiv of $LiN(CH_3)(C_6H_5)$ in THF results in the formation of platinum(II) amide complexes (eq 1). Isolation is accomplished by solvent removal followed by extraction with benzene or $CH_2Cl_2$. Concentration of the solutions followed by precipitation with hexane allows isolation of air-sensitive yellow platinum(II) amide complexes in greater than 65% yields. Similarly, the reaction of $LiN(CH_2C_6H_5)(H)$ with (DPPE)$PtCH_3(Cl)$ yields (DPPE)$Pt(CH_3)[N(CH_2C_6H_5)(H)]$.[4] Using $LiN(CH_3)_2$ in place of $LiN(CH_3)C_6H_5$ at low temperature resulted in the formation of unstable dimethylamide complexes which decompose above 0 °C. These species have not been isolated in pure form.

$$L_2PtRCl + LiNCH_3(C_6H_5) \rightarrow L_2PtR[NCH_3(C_6H_5)] \quad (1)$$

(DPPE)$Pt(CH_3)[N(CH_2C_6H_5)(H)]$ reacts with 3 atm of CO at 25 °C to give (DPPE)$Pt(CH_3)[C(O)NCH_2C_6H_5(H)]$ in 80% yield. Similarly, the reaction of (DPPE)Pt-$(CH_3)(N(CH_3)_2)$ (generated in situ) with CO leads to (DPPE)$Pt(CH_3)[C(O)N(CH_3)_2]$ in 76% isolated yield. Although the reactions of CO with the Pt–$N(CH_3)(C_6H_5)$ complexes reported in this paper appear to give analogous insertion products, we have not been able to isolate them because deinsertion in these cases appears to be facile. There is no evidence for insertion into the Pt–C bond. These are the first examples of CO insertion into late transition metal–nitrogen bonds and these transformations

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[†] Contribution No. 3606.

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(3) (DMPE)$PtCH_3(NC_6H_5(CH_3))$ crystallizes from THF/hexane in space group $P2_1/n$ with cell dimensions $a$ = 6.2790 (8) Å, $b$ = 16.111 (2) Å, $c$ = 16.894 (2) Å, and $\beta$ = 96.47(1) with $Z$ = 4. In this structure the trigonal plane of nitrogen is 68° out of the coordination plane of platinum. Additional information is available as supplementary material.

(4) Proton NMR of complexes in THF-$d_8$ unless otherwise noted. (DPPE)$Pt(CH_3)[NCH_3(C_6H_5)]$: $\delta$ 7.80 (m, 4 H), 7.69 (m, 4 H), 7.48 (m, 6 H), 7.30 (m, 6 H), 6.69 (t, $J$ = 8 Hz, 2 H), 6.48 (d, $J$ = 8 Hz, 2 H), 5.91 (t, $J$ = 7 Hz, 1 H), 5.37 (d, $J$ = 3.4 Hz, $J_{Pt}$ = 34 Hz, 3 H), 2.3 (m, 4 H), 0.52 (dd, $J$ = 4.7, 7.8 Hz, $J_{Pt}$ = 64 Hz, 3 H). (DMPE)$Pt(CH_3)[NCH_3(C_6H_5)]$: $\delta$ 6.72 (t, $J$ = 7.5 Hz, 2 H), 6.40 (d, $J$ = 7.5 Hz, 2 H), 5.90 (t, $J$ = 7.6 Hz, 1 H), 2.8 (d, $J$ = 3 Hz, $J_{Pt}$ = 32 Hz, 3 H), 1.8 + 1.5 (m, m, 4 H), 1.55 (d, $J$ = 10 Hz, $J_{Pt}$ = 37 Hz, 6 H), 1.30 (d, $J$ = 9 Hz, $J_{Pt}$ = 17 Hz, 6 H), 0.35 (dd, $J$ = 8, 5 Hz, $J_{Pt}$ = 62 Hz). (DPPE)PtPh($NPhCH_3$): $\delta$ 7.7 (m, 4 H), 7.6 (m, 4 H), 7.4 (m, 12 H), 7.03 (m, 2 H), 6.5 (m, 5 H), 6.45 (d, $J$ = 8 Hz, 2 H), 5.79 (t, $J$ = 7 Hz, 1 H), 2.5 (d, $J$ = 3 Hz, $J_{Pt}$ = 36 Hz, 3 H), 2.35 (m, 4 H). (DPPE)$Pt(CH_2Ph)(NPhCH_3)$: $\delta$ 7.77 (m, 4 H), 7.50 (br s, 8 H), 7.25 (m, 6 H), 6.60 (m, 4 H), 6.40 (d, $J$ = 6 Hz, 2 H), 5.90 (t, $J$ = 7 Hz, 1 H), 2.74 (dd, $J$ = 10, 6 Hz, $J_{Pt}$ = 90 Hz, 2 H), 2.31 (d, $J$ = 4 Hz, $J_{Pt}$ = 31 Hz, 3 H), 2.3 + 2.1 (m, 4 H). (DPPE)$Pt(CH_3)[NH(CH_2Ph)]$: $\delta$ 8.0 (m, 4 H), 7.7 (m, 4 H), 7.4 (m, 12 H), 7.14 (d, $J$ = 6 Hz, 2 H), 7.04 (t, $J$ = 6 Hz, 2 H), 6.94 (t, $J$ = 6 Hz, 1 H), 4.28 (dd, $J$ = 4, 8 Hz, $J_{Pt}$ = 33 Hz, 2 H), 0.78 (t, $J$ = 7 Hz, $J_{Pt}$ = 69 Hz, 1 H), 0.32 (dd, $J$ = 5, 7 Hz, $J_{Pt}$ = 65 Hz, 3 H). (DPPE)$Pt(CH_3)[C(O)N(CH_3)_2]\cdot$THF: $^1$H NMR ($\delta$, $CD_2Cl_2$) 0.54 (dd, $J$ = 6.9, 8.2, $J_{Pt}$ = 72 Hz, 3 H), 2.69 (s, $J_{Pt}$ = 5.4 Hz, 3 H), 2.72 (s, 3 H), 8.1 (m) + 7.8 (m) + 7.5 (m) (20 H), and 2.55 (m) + 2.15 (m) (4 H) along with THF resonances. (DPPE)$PtCH_3[C(O)NCH_2Ph(H)]$: $\delta$ 5.68 (t, $J$ = 5.4 Hz, 1 H), 4.25 (d, $J$ = 5.7 Hz, 2 H, with unresolved Pt satellite), 2.3 (m, 4 H), 0.74 (dd, $J$ = 7, 8 Hz, $J_{Pt}$ = 72 Hz, 3 H) and aromatic protons. Elemental analyses and other spectral data on these complexes are available as supplementary material.

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bear formal similarity with insertion of CO into Pt–O bonds of analogous platinum alkoxides.[5]

(DPPE)Pt($CH_3$)[$NCH_3(C_6H_5)$], **1**, rapidly reacts with acetyl chloride at 25 °C to yield (DPPE)Pt($CH_3$)(Cl) and *N*-methyl-*N*-phenylacetamide. This nucleophilicity appears general; for example, **1** reacts cleanly with $CD_3I$ to give (DPPE)Pt($CH_3$)(I) and ($C_6H_5$)N($CH_3$)($CD_3$) as identified by $^1H$, $^2H$, and $^{31}P$ NMR and mass spectral analysis.[6] Complex **1** reacts analoguously to Pt(II) alkoxide complexes toward weak acids;[7] acetone, phenylacetylene, and acetonitrile all react with **1** to give *N*-methylaniline. The organometallic products, in these cases, are (DPPE)Pt($CH_3$)(X) (X = $CH_2COCH_3$, CCPh, $CH_2CN$).

Our study of the equilibrium between (DPPE)Pt$CH_3$($OCH_3$) and $HNCH_3(C_6H_5)$ (eq 2) indicates the above reactions do not involve free amide formed by dissociation.

$$\text{(DPPE)PtCH}_3\text{(OCH}_3\text{)} + \text{HNCH}_3\text{(C}_6\text{H}_5\text{)} \rightleftharpoons \text{(DPPE)PtCH}_3\text{[NCH}_3\text{(C}_6\text{H}_5\text{)]} + \text{HOCH}_3 \quad (2)$$

The measured equilibrium constant of 0.8 shows the reaction to be nearly thermoneutral.[9] This information, evaluated with p$K_a$ data, shows dissociation of methylphenylamide has an activation barrier of at least 39 kcal/mol in THF solution.[10] Interestingly, the X–H bond dissociation energies of methanol and *N*-methylaniline, combined with the thermoneutral character of eq 2 demonstrate the Pt–O bond is stronger, with respect to homolytic cleavage, than the Pt–N bond by about 16.5 kcal/mol; roughly the same as the difference between the relevant O–H and N–H bonds.[11]

In summary, we have prepared a number of platinum(II) amide complexes and have investigated their chemistry. While these species prove strong nucleophiles, they do not require dissociation of free amide to react with electrophiles. The weak Pt–N bond, relative to the Pt–O bonds, may explain the greater reactivity of late-transition-metal amide complexes than of analogous alkoxides and suggests a wealth of catalytic chemistry involving metal amides may be possible.

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**Registry No.** 1, 95465-07-9; (DMPE)Pt$CH_3$($NC_6H_5(CH_3)$), 95465-08-0; (DPPE)PtPh($NPhCH_3$), 95465-09-1; (DPPE)Pt($CH_2Ph$)($NPhCH_3$), 95465-10-4; (DPPE)Pt($CH_3$)[NH($CH_2Ph$)], 95482-63-6; (DPPE)Pt($CH_3$)[C(O)$NCH_2C_6H_5$(H)], 95465-11-5; (DPPE)Pt($CH_3$)(N($CH_3)_2$), 95465-12-6; (DPPE)Pt($CH_3$)[C(O)N($CH_3)_2$], 95465-13-7; (DPPE)Pt($CH_3$)(I), 27711-52-0; ($C_6H_5$)N($CH_3$)($CD_3$), 88889-00-3; (DPPE)Pt($CH_3$)($CH_2COCH_3$), 43210-96-4; (DPPE)Pt($CH_3$)CCPh), 65310-61-4; (DPPE)Pt($CH_3$)($CH_2CN$), 43210-97-5; (DMPE)Pt($CH_3$(Cl), 95465-14-8; (DPPE)Pt$CH_3$(Cl), 27711-50-8; (DPPE)PtPh(Cl), 27711-51-9; (DPPE)Pt$CH_2Ph$(Cl), 65310-81-8; (DPPE)Pt$CH_3$($OCH_3$), 82405-05-8; $HNCH_3(C_6H_5)$, 100-61-8; LiN($CH_3$)($C_6H_5$), 35954-01-9; LiN($CH_2C_6H_5$)(H), 38225-27-3; LiN($CH_3)_2$, 3585-33-9; $CD_3I$, 865-50-9; $HNCH_3(C_6H_5)$, 100-61-8; acetyl chloride, 75-36-5; acetone, 67-64-1; phenylacetylene, 536-74-3; acetonitrile, 75-05-8; *N*-methyl-*N*-phenylacetamide, 579-10-2.

**Supplementary Material Available:** Additional information on the crystal structure of (DMPE)Pt$CH_3$[$NCH_3(C_6H_5)$] and elemental analyses and spectral data on complexes reported in this paper (11 pages). Ordering information is given on any current masthead page.

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[6] We cannot, at this time, rule out a mechanism involving initial oxidative addition of the alkyl or acyl halide to the Pt(II) starting material followed by stereospecific reductive elimination; however, the singular products obtained suggest this is not the case.

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[8] The equilibrium constant was measured by $^1H$ NMR experiments in THF-$d_8$ solvent. Equilibration was complete after 2 weeks at room temperature and was measured as 0.8 ± 0.1.

[9] Complex 1 can be isolated in 62% yield by combining 10 equiv of *N*-methylaniline with (DPPE)Pt($CH_3$)($OCH_3$). For an analogous reaction of Pt–OH with *N*-methylaniline see: Michelin, R. A.; Napoli, M. *J. Organomet. Chem.* **1979**, *175*, 239.

[10] The *upper limit* of methoxide dissociation from (DPPE)Pt$CH_3$($OCH_3$) at 25 °C in THF-$d_8$ has been established as $1 \times 10^{-7}$ $s^{-1}$ ($\Delta G^\ddagger >$ 27 kcal/mol). From the equilibrium constant of eq 2 and the relative p$K_a$'s of methanol and methylaniline, the rate of amide dissociation from 1 must be slower than $1 \times 10^{-6}$ $s^{-1}$ at 25 °C in THF ($\Delta G^\ddagger > 39$ kcal/mol).

[11] Bond dissociation energies of 87.5 kcal/mol (H–$NCH_3C_6H_5$) and 104 kcal/mol (H–$OCH_3$) were taken from: Golden, D.; McMullen, D. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. We are grateful to Professor R. G. Bergman for bringing this review to our attention.

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# Monomeric and Dimeric Niobium(II) and Niobium(III) Cyclopentadienyl Carbonyl and Alkyne Complexes

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*Summary:* Aluminum powder reduces $CpMCl_4$ (M = Nb, Ta) in the presence of 1–4 atm of CO in THF to give the dimers $Cp_2M_2(CO)_4Cl_2(\mu\text{-}Cl)_2$. In the presence of di-*p*-tolylacetylene, $Cp'NbCl_4$ is reduced by Al to give the monomeric alkyne complex $Cp'Nb(ArCCAr)Cl_2$ (**4**). The Nb(III) complexes are reduced with Na/Hg to give Nb(II) dimers with a Nb–Nb bond: $Cp'_2Nb_2(CO)_4(\mu\text{-}Cl)_2$ (**5**) and $Cp'_2Nb_2(ArCCAr)_2(\mu\text{-}Cl)_2$ (**6**). The $^{13}C$ NMR chemical shifts of the acetylenic carbons in **4** and **6** (216 and 214 ppm) suggest that the alkyne donates 4 electrons to the Nb atoms. The structures of **5** and **6** are dramatically different; **5** has a folded $Nb_2Cl_2$ core whereas **6** has a centrosymmetric structure with a planar $Nb_2Cl_2$ core.

We have synthesized new, low-valent organometallic complexes of Nb and Ta as part of our investigations on the chemistry of metal–metal multiple bonds.[1,2] The compounds $CpM(CO)_3Cl_2$ (**1**) (M = Nb, Ta), which were reported[3] to be the products of the Al reduction of $CpMCl_4$ under 1 atm of CO, offer considerable promise as convenient starting materials for metal–metal bonded complexes. Furthermore, the Al reduction procedure might be extended to give a general synthesis of Nb(III) and

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