Organometallics **1999,** *18,* 297−299

Lewis Acids Accelerate Reductive Elimination of RCN from $P_2Pd(R)(CN)$

Jinkun Huang, Christopher M. Haar, and Steven P. Nolan[†]

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

John E. Marcone and Kenneth G. Moloy*[,‡]

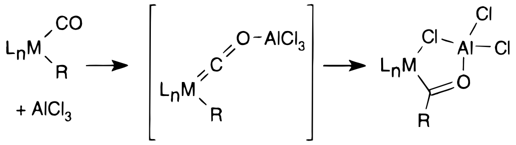
Central Research and Development, E. I. du Pont de Nemours & Co., Inc.,
Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880-0328[§]

Received November 2, 1998

Summary: The rate of reductive elimination of the complexes dpppPd(CH_2TMS)($CNER_3$) ($E = B$, Al) is accelerated up to 60-fold over dpppPd(CH_2TMS)(CN). Based on kinetic considerations and the isoelectronic relationship of CN^- and CO, a migration-type mechanism for reductive elimination is proposed. The rate acceleration correlates directly with Lewis acid strength, the latter determined by solution calorimetric analyses of the Lewis acid adduct forming reaction $Pd-CN + ER_3 \rightarrow Pd-CN-ER_3$.

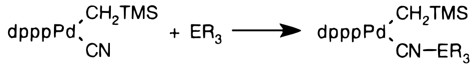
Reductive elimination is a key transformation in organometallic chemistry which quite often represents the product-forming, and sometimes rate-determining, step in a number of important stoichiometric and catalytic reactions.[1] While the importance of reductive elimination is clear, quantitative descriptions of this process are not as well developed as those of other elementary organometallic transformations.[1a,2] Through an exploration of the factors that influence the reductive elimination process, such as the effects of ancillary ligands and the functional groups undergoing reductive elimination, our current efforts are directed toward developing a more complete model for this fundamental process.[3,4]

We recently reported a kinetic and mechanistic analysis of reductive elimination of RCN from the complexes (diphosphine)Pd(R)(CN) (R = CH_2TMS, CH_2CMe_3).[3] The rate was shown to depend strongly on the diphosphine bite angle, spanning a range of nearly 10^4 from diphos (bite angle ≈ 85°) to DIOP (bite angle ≈ 100°).[5] The rate was also found to depend on the alkyl group, with this parameter also causing the rate to vary by orders of magnitude ($CH_2CMe_3 \approx 10 \times CH_2TMS \gg CH_3$). A mechanism involving migration of the alkyl group to cyanide in the rate-determining C−C bond-forming step was proposed. This mechanism is similar to that proposed for other reductive elimination reactions (C−C, C−H, and Si−H formation)[1b,6] and is somewhat analogous to the familiar migratory insertion of CO, with which cyanide is isoelectronic. Lewis acids have been shown to greatly accelerate migratory CO insertions, presumably via adduct formation with coordinated CO, as shown in eq 1.[7] Lewis acids show analogous behavior with metal cyanides, and complexes of the type M−CN−LA are well-known.[8] Furthermore, because Lewis acids are used commercially as promoters in olefin hydrocyanation, the possible influence of Lewis acids on reductive elimination in the present system is of significant practical interest.[9] These considerations lead us to consider the possible influence of Lewis acids on reductive elimination from (diphosphine)Pd(R)(CN).



(1)

The Lewis acid adducts dpppPd(CH_2TMS)($CNER_3$) are generated upon combination of the reagents according to eq 2. These adducts are readily isolated as colorless, crystalline complexes and show the expected spectroscopic properties.[10] Notably, ν_{CN} increases sub-



(2)

$ER_3 = BEt_3, AlEt_3, BPh_3, B(C_6F_5)_3, AlPh_3$

[†] E-mail: snolan@uno.edu.

[‡] E-mail: moloykg@esvax.email.dupont.com.

[§] Contribution No. 7793.

[1] (a) Goldberg, K. I.; Yan, J.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889, and references therein. (b) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1031, and references therein. (c) Byers, P. K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D. *Organometallics* **1988**, *7*, 1363, and references therein. (d) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.

[2] Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985; p 177.

[3] Marcone, J. E.; Moloy, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 8527.

[4] A detailed study of the factors influencing C−S bond-forming reductive elimination has recently appeared: Mann, G.; Baranano, D.; Hartwig, J. F.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 9205.

[5] Abbreviations: diphos = $Ph_2P(CH_2)_2PPh_2$; dppp = $Ph_2P(CH_2)_3PPh_2$; DIOP = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.

[6] (a) Calhorda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*, 1431. (b) Cleary, B. P.; Mehta, R.; Eisenberg, R. *Organometallics* **1995**, *14*, 2297, and references therein. (c) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478.

[7] Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219.

[8] (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 253−255. (b) Woodcock, C.; Shriver, D. F. *Inorg. Chem.* **1986**, *25*, 2137, and references therein.

[9] a) Tolman, C. A.; McKinney, R. J.; Seidel, W. C.; Druliner, J. D.; Stevens, W. R. *Adv. Catal.* **1985**, *33*, 1. (b) McKinney, R. J.; Nugent, W. A. *Organometallics* **1989**, *8*, 2871.

[10] See Supporting Information for complete details.

10.1021/om980897x CCC: $18.00
Publication on Web 01/14/1999

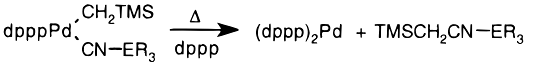
Table 1. Lewis Acid-Accelerated Reductive Elimination from dpppPd(CH_2TMS)(CN)[a]

Lewis acid	ν_{CN} (cm^{-1})	k,[b] eq 3 (s^{-1})	$\Delta H^{\ddagger}$, eq 3 (kcal/mol)	$\Delta S^{\ddagger}$, eq 3 (eu)	$-\Delta H$,[c] eq 2 (kcal/mol)
none	2123	$5.8(6) \times 10^{-6}$	27.3(1.2)	−1(3)	n/a
BEt_3	2189	$1.2\ (3) \times 10^{-5}$	32.6(1.4)	16(3)	13.2 (2)
BPh_3	2195	$3.3\ (3) \times 10^{-5}$			15.2 (1)
$AlEt_3$	2165	$1.2\ (2) \times 10^{-4}$			32.5 (1)
$B(C_6F_5)_3$	2203	$1.3\ (2) \times 10^{-4}$			31.2 (2)
$AlPh_3$	2165	$3.4\ (6) \times 10^{-4}$	25.0(1.1)	0(3)	36.9 (2)

[a] Values in parentheses represent the error in the last significant digit (3σ for k and $-\Delta H$, 1σ for activation parameters). [b] Rate constants are given for the common temperature of 62 °C. With the exception of the first entry (THF-d_8) all kinetic experiments were conducted in toluene-d_8. [c] Enthalpy values for AlR_3 are corrected for the equilibrium $Al_2R_6 \leftrightarrow 2AlR_3$.[12]

stantially upon adduct formation (Table 1), as expected.[11] The structures of two members of this series have been confirmed by X-ray crystallography (ER_3 = BEt_3, $AlEt_3$), and these details will be published separately.

Thermolysis of dpppPd(CH_2TMS)($CNER_3$) at ca. 60 °C (toluene-d_8) leads to formation of $TMSCH_2CN$-ER_3 and Pd(0), according to eq 3. The latter is trapped as



$$\text{dpppPd}\begin{matrix}\text{CH}_2\text{TMS}\\ \text{CN}-\text{ER}_3\end{matrix} \xrightarrow[\text{dppp}]{\Delta} (\text{dppp})_2\text{Pd} + \text{TMSCH}_2\text{CN}-\text{ER}_3 \qquad (3)$$

$(dppp)_2Pd$ by performing the reaction in the presence of added dppp. Kinetic measurements (^1H NMR) show that reductive elimination is first order in dpppPd(CH_2TMS)($CNER_3$) and zero order in excess dppp. This behavior is identical to that observed in the absence of Lewis acid, e.g., with dpppPd(CH_2TMS)(CN).[3] The kinetic studies were also conducted with excess Lewis acid both to eliminate trace amounts of water and to avoid complications resulting from potential equilibrium dissociation of the Lewis acid (the reverse of eq 2). For all of the Lewis acids studied, varying the ER_3/Pd ratio from 7.5 to 20 had no effect on the measured rate constants. The rate is also insensitive to solvent. Thus, thermolysis of dpppPd(CH_2TMS)($CNAlPh_3$) proceeds with a rate constant of $9.0(0.1) \times 10^{-5}\ s^{-1}$ in toluene-d_8 at 51.5 °C. In THF-d_8 the measured rate constant is $5.9(0.1) \times 10^{-5}\ s^{-1}$.

The Lewis acid adducts undergo reductive elimination at faster rates than the parent complex. The greatest acceleration is exhibited by dpppPd(CH_2TMS)($CNAlPh_3$), which shows a 60-fold increase in rate relative to dpppPd(CH_2TMS)(CN).

To quantitatively gauge and rank the acidity of the Lewis acids ER_3 with respect to the base (Pd−CN) used in this study, we investigated the thermodynamics of adduct formation as depicted in eq 2. The enthalpy of this reaction is conveniently measured by anaerobic solution calorimetry, using techniques previously reported.[12] The reaction enthalpies in the present system are found to span a ca. 25 kcal/mol range (Table 1). The relative ranking is as expected: Al is a stronger acid than B and EPh_3 is slightly more acidic than EEt_3.[13] The pronounced Lewis acidity of $B(C_6F_5)_3$ is clearly evident, rendering boron approximately equal in acidity to aluminum. The palladium−cyanide complex is, not unexpectedly,[14] a significantly stronger base than the organic nitrile, as shown by the result in eq 4.

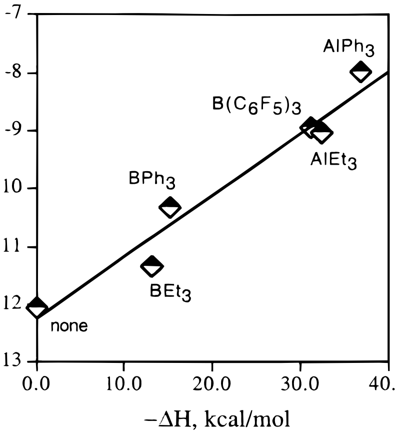


Figure 1. Correlation of reductive elimination rate with Lewis acidity for dpppPd(CH_2TMS)($CNER_3$); data from Table 1.

$$\text{TMSCH}_2\text{CN} + \text{AlPh}_3 \longrightarrow \text{TMSCH}_2\text{CNAlPh}_3 \qquad \Delta H = -24.2\ (1)\ \text{kcal/mol} \qquad (4)$$

As shown in Figure 1, the reductive elimination rate (eq 3) correlates very well with the enthalpy of reaction 2. The coordination of Lewis acids to metal cyanides is known to induce positive charge formation at nitrogen and carbon (relative to the M−CN free base), with concomitant negative charge formation at boron or aluminum.[11e] The nitrile carbon is consequently rendered more susceptible to nucleophilic attack by the alkyl group, thus explaining the rate acceleration in the Lewis acid adducts.

Our proposed mechanism involves rate-determining migration of the alkyl group to the bridging cyanide, followed by dissociation of the adduct $RCNER_3$ (Scheme 1). This migration-like mechanism is similar to that proposed for other reductive eliminations,[1b,6] and also that proposed by us for reductive elimination from the parent complexes (diphosphine)Pd(R)(CN).[3] This proposal is supported by the kinetics which indicates an intramolecular process on the path to the transition state. The small, favorable $\Delta S^{\ddagger}$ (0 to +16 eu) is consistent with either reduced steric congestion in the transition state or partial product dissociation. Full product dissociation would be expected to result in a much more

---

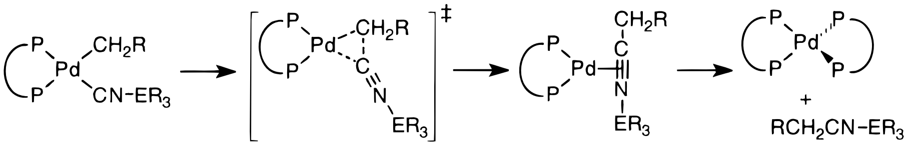
[11] Coordination of Lewis acids to metal cyanides results in strengthening of the CN σ bond, and renders cyanide a better π acceptor. The σ bond strengthening is responsible for the increase in ν_{CN} upon Lewis acid adduct formation. The subsequent decrease in ν_{CN} as the Lewis acidity is increased is likely attributable to the accompanying increase in metal-to-ligand back-bonding. (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986; p 272. b) Drago, R. S. Physical Methods in Chemistry; W. B. Saunders: Philadelphia, 1977; p 177. (c) Kristoff, J. S.; Shriver, D. F. *Inorg. Chem.* **1973**, *12*, 1788. (d) Shriver, D. F.; Swanson, B. *Inorg. Chem.* **1971**, *10*, 1354. (e) Purcell, K. F.; Drago, R. S. *J. Am. Chem. Soc.* **1966**, *88*, 919.

[12] (a) Nolan, S. P.; Hoff, C. D.; Landrum, J. T. *J. Organomet. Chem.* **1985**, *282*, 357. (b) Nolan, S. P.; Lopez de la Vega, R.; Hoff C. D. *Inorg. Chem.* **1986**, *25*, 4446.

[13] The calorimetric values reported for AlR_3 are corrected for the equilibrium $Al_2R_6 = 2\ AlR_3$. $AlPh_3$: (a) Govorchin, S. W.; Kana'an, A. S. *J. Chem. Thermodyn.* **1984**, *16*, 437. (b) Galuashvili, Zh. S.; Romm, I. P.; Gur'yanova, E. N.; Korneev, N. N. Kocheshkov, K. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 2713. $AlEt_3$: (c) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, A., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 1, Chapter 6, p 593.

[14] Shriver, D. F. *J. Am. Chem. Soc.* **1963**, *85*, 1405.

Scheme 1



significant contribution from $T\Delta S^{\ddagger}$ (>10 kcal/mol vs the 0–5 kcal/mol range observed here), and thus the coupled product likely remains substantially bound in the transition state. Although rate-determining product dissociation from the proposed intermediate η^2-nitrile cannot be ruled out, the substitutional lability of nitrile complexes in general and of the complexes P_2PdL in particular[15] suggests that this is unlikely. The experimental results are not consistent with a mechanism involving dissociation of $CNER_3^-$, followed by attack of this anion on the alkyl group. Such a mechanism has been proposed in the case of CH_3I elimination from six-coordinate, d^6 dppePt$(CH_3)_3$I.[1a] Thus, in the present case the rate is negligibly dependent on solvent (toluene vs THF). Also, the excess Lewis acid employed during the rate measurements would be expected to have an inhibitory effect due to formation of the known anions $R_3ECNER_3^-$ if R_3ENC^- dissociation were operable and $R_3ECNER_3^-$ were formed irreversibly.[16]

In conclusion, we have shown that reductive elimination of RCN can be significantly enhanced with Lewis acids. This represents a third parameter that governs reductive elimination rates in this class of molecules. In the single case of $P_2Pd(R)(CN)$, we have demonstrated that variation of R, the diphosphine bite angle, and the use of Lewis acids can cause the elimination rate to vary by at least 6 orders of magnitude.[17] Further studies of the parameters influencing this fundamental transformation are in progress.

Acknowledgment. We thank Ms. L. A. Howe for expert assistance with the kinetics measurements. Helpful discussions with Drs. R. D Simpson and V. Grushin are gratefully acknowledged. S.P.N. acknowledges the National Science Foundation (CHE-9631611) for partial support of this research.

Supporting Information Available: Text describing synthetic, spectroscopic, and analytical data for the complexes dpppPd(R)($CNER_3$) and details regarding the kinetic measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980897X

---

(15) (a) Kranenburg, M.; Delis, J. G. P.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Vrieze, K.; Veldman, N.; Spek, A. L.; Goubitz, K.; Fraanje, J. *J. Chem. Soc., Dalton Trans.* **1997**, 1839. (b) Portnoy, M.; Ben-David, Y.; Rousso, I.; Milstein, D. *Organometallics* **1994**, *13*, 3465.

(16) Lippard reports[15a] that $Ph_3BCNBPh_3^-$ indeed dissociates Ph_3B at elevated temperature. The greater acidity of AlR_3 and $B(C_6F_5)_3$ makes dissociation less likely for the analogous species $R_3ECNER_3^-$. (a) $Ph_3BCNBPh_3^-$: Giandomenico, C. M.; Dewan, J. C.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 1407. (b) $Me_3AlCNAlMe_3^-$: Weller, F.; Dehnicke, K. *J. Organomet. Chem.* **1972**, *36*, 23.

(17) This conclusion assumes the effects are additive.