Kinetic Study of Reductive Elimination from the Complexes (Diphosphine)Pd(R)(CN)

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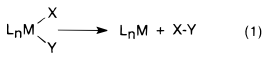
Received March 9, 1998

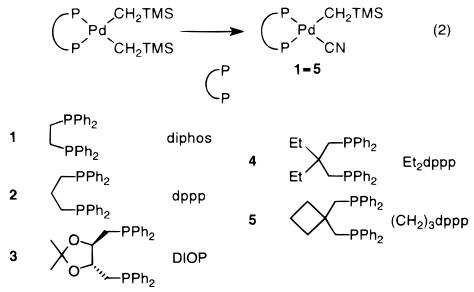
The reductive elimination reaction (eq 1) is a key transformation in organometallic chemistry, often representing both the product-forming and rate-determining steps in a number of important transformations, both stoichiometric and catalytic.[1] Examples include chemistries as varied as hydrogenation, hydroformylation, carbonylation, hydrocyanation, and coupling reactions.[2] While the importance of this transformation is clear,



(1)

a quantitative understanding is not as well developed as other fundamental reactions in organometallic chemistry,[1a,3] although C−H, Si−H, and C−C elimination have received significant attention.[1,4] The effect of ancillary ligands on the energetics of reductive elimination is lacking to a significantly greater degree. This latter point is particularly important, as chelating diphosphines with large bite angles have recently been shown to be especially beneficial in a number of important catalytic reactions and these ligands are now receiving a great deal of attention.[5−7] In several cases it is speculated that large bite angle diphosphines accelerate reaction rates by enhancing the rates of product-forming reductive elimination,[5a−d,8] and two prior studies offer evidence for this conclusion.[5c,9] We have found that reductive elimination of RCN from the complexes (diphosphine)Pd(R)(CN) (R = CH_2-TMS, CH_2CMe_3) provides a unique opportunity to study the kinetics of this important transformation and a quantitative measure of how it is influenced by the chelating diphosphine. These complexes also serve as models for two important transformations: nickel-catalyzed olefin hydrocyanation[10] and palladium-catalyzed coupling reactions.[8]

The complexes (diphosphine)Pd(R)(CN) are prepared via the route shown in eq 2. The synthesis of the dialkyl precursors follows procedures described for similar complexes.[11] Conversion



of the dialkyls to the alkyl cyanide complexes is accomplished by one of two methods: treatment with CF_3CO_2H, followed by Bu_4NCN, or by direct reaction with excess HCN.[12] Complexes **1**−**5** present a series wherein the chelate ring size/bite angle is methodically changed while maintaining constant donor properties at phosphorus, as shown by IR.[13]

Heating a colorless solution of complex **1** and ≥1.5 equiv of diphos in THF-d_8 leads to quantitative formation of $TMSCH_2CN$ and bright yellow Pd(diphos)$_2$, as determined by ^{1}H and ^{31}P NMR monitoring. A kinetic analysis shows the reaction is first order in **1** and is independent of the excess diphos concentration, for >5 half-lives. Events leading to the transition state are thus intramolecular, and the excess ligand serves only to trap Pd(0). The formation rate of $TMSCH_2CN$ is equal to the decay rate of **1**. Kinetic analyses of reductive elimination from complexes **2**−**5** were also conducted. As with **1**, all experiments were conducted in the presence of a small excess of the appropriate diphosphine. The entire series exhibits first-order decay in [Pd(alkyl)(cyanide)] and zero-order dependencies on the excess diphosphine. All kinetic runs showed clean formation of $TMSCH_2CN$ and Pd(diphosphine)$_2$, the latter confirmed by independent generation from Pd_2dba_3 and 4 equiv of diphosphine.[14]

The reductive elimination rate increases significantly with increasing diphosphine bite angle (Table 1). Thus, progressing from the small bite angle (∼85°[7b]) ligand diphos in **1** to the larger bite angle of DIOP (∼100°[7b]) in **3** results in a nearly 10^4-fold rate increase. Complex **2**, with an intermediate bite angle (dppp, ∼90°[7b]), lies between these two extremes. Because the substituents at phosphorus are essentially identical throughout this series the kinetic ordering is attributable to changes in the chelate ring size and is not electronic in origin.[15] Increasing chelate ring size results in increased bite angles, chelate flexibility, and steric size, and all would be expected to enhance reductive elimination in the present case. These factors favor both a mechanism involving an intact chelate ring (where ∠PPdP is ideally larger in the transition state than in the square planar starting material) or one involving preequilibrium chelate ring opening. Increasing the

(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) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organometallic Chemistry*; University Science Books: Mill Valley, CA, 1987. (c) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985.

(3) Reference 2c, p 177.

(4) Cleary, B. P.; Mehta, R.; Eisenberg, R. *Organometallics* **1995**, *14*, 2297, and references therein.

(5) Coupling reactions: (a) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217. (b) Kranenburg, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **1998**, 155. (c) Brown, J. M.; Guiry, P. J. *Inorg. Chim. Acta* **1994**, *220*, 249. (d) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158. (e) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232. (f) Mann, G.; Hartwig, Driver, J. F.; M. S.; Fernández-Rivas, C. *J. Am. Chem. Soc.* **1998**, *120*, 827. (g) Widenhofer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787.

(6) Hydrocyanation: Goertz, W.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Vogt, D. *J. Chem. Soc., Chem. Commun.* **1997**, 1521.

(7) Hydroformylation: (a) Kranenburg, M.; van der Burgt, Y. E. M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J. *Organometallics* **1995**, *14*, 3081. (b) Casey, C. P.; Whiteker, G. T.; Melville, M. G.; Petrovich, L. M.; Gavney, J. A., Jr.; Powell, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 5535.

(8) Calhorda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*, 1431.

(9) Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1980**, *192*, 265.

(10) (a) Tolman, C. A.; McKinney, R. J.; Seidel, W. C.; Druliner, J. D.; Stevens, W. R. *Adv. Catal.* **1985**, *33*, 1. (b) Bäckvall, J. E.; Andell, O. S. *Organometallics* **1986**, *5*, 2350.

(11) (a) Diversi, P.; Fasce, D.; Santini, R. *J. Organomet. Chem.* **1984**, *269*, 285. (b) Tooze, R.; Chiu, K. W.; Wilkinson, G. *Polyhedron* **1984**, *3*, 1025.

(12) The complex DIOPPd(CN)(Et) has been prepared from $DIOPPdEt_2$ and excess HCN: Hodgson, M.; Parker, D.; Taylor, R. J.; Ferguson, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1309.

(13) IR data (ν_{CN} in CH_2Cl_2, cm^{-1}): **1**, 2127; **2**, 2123; **3**, 2126; **4**, 2123; **5**, 2126; diphosPd(CH_2CMe_3)(CN), 2119.

(14) Amatore, C.; Broecker, G.; Jutand, A.; Khalil, F. *J. Am. Chem. Soc.* **1997**, *119*, 5176.

(15) Changing ∠PPdP will almost certainly have some effect on the electronics at palladium; it is only suggested that the donor/acceptor properties of the phosphorus ligands are held nearly constant.

S0002-7863(98)00762-8 CCC: $15.00
Published on Web 08/05/1998

Table 1. Rate Data and Activation Parameters for Reductive Elimination of RCN from the Complexes (diphosphine)Pd(R)(CN)

Complex	k at 80 °C (s^{-1})[a,b]	$\Delta H^{\ddagger}$ (kcal mol^{-1})[c]	$\Delta S^{\ddagger}$ (e.u.)[c]	temp range (°C)
1	2.1(0.2)e-6	30.8(3)	2.3(8)	85−119
2	5.0(0.7)e-5	27.3(1.2)	−1(3)	60−98
3	1.0(0.2)e-2	28.2(0.4)	12(1)	36−60
4	2.1(0.1)e-5	32.9(0.6)	13(2)	65−94
5	7.4(0.7)e-5	32.5(0.9)	14(3)	60−94
diphosPd (CH_2CMe_3)(CN)	2.6(0.1)e-5	28.7(0.5)	1(2)	66−87

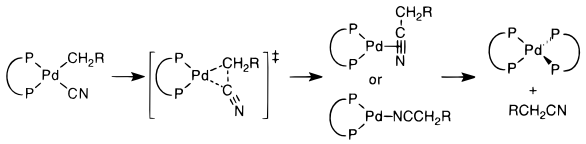
[a] Rate constants at the common temperature of 80 °C are calculated by interpolation or extrapolation of linear regressions of the Eyring data (see the Supporting Information). [b] Values in parantheses are 95% confidence limits. [c] Values in parantheses are the standard error.

diphosphine bite angle and sterics compresses the ∠CPdC, forcing the two carbon atoms closer together, and this would also be expected to accelerate C−C bond formation and subsequent elimination.[16] Enhanced reductive elimination rates with increasing bite angle has been previously suggested[5c] but quantified only in the case of (diphosphine)Ni(CH_3)$_2$, where elimination of ethane is 50 times faster for dppp than for diphos, similar to that observed here.[9] Computational studies indicate that reductive elimination proceeds with reduced barriers when ∠PPdP in hypothetical *cis*-(PH_3)$_2$Pd(CH_3)(CH═CH_2) is allowed to increase along the reaction coordinate.[8]

The rate law and activation parameters ($\Delta S^{\ddagger}$) rule out a mechanism involving coordination of excess phosphine to give an 18 e intermediate which then reductively eliminates product.[17] However, the kinetic data do not distinguish between mechanisms involving four-coordinate (16 e) or three-coordinate (14 e) intermediates, the latter involving dissociation of one arm of the diphosphine chelate. The ligand dissociation preequilibrium mechanism is generally favored with related monophosphine d^8 complexes such as (R_3P)$_2$M(X)(Y) (M = Ni, Pd, Pt), and (R_3P)-Au(R′)$_3$.[1d,2,5e,18] Both mechanisms are consistent with the observed kinetic ordering with respect to chelate ring size. Exchange of the inequivalent P nuclei in complexes **1**−**5** is not observed by ^{31}P NMR during the course of the reductive elimination, but the time scale of this experiment is of no use for discriminating the two mechanisms.[19]

An attempt to distinguish these mechanisms has been made through the use of *gem*-dialkyl and Thorpe−Ingold effects.[21] *gem*-Dialkyl substitution is known to greatly enhance and stabilize ring formation in organic ring systems. The new ligands Et_2-dppp and (CH_2)$_3$dppp were prepared to investigate the effect of *gem*-dialkyl substitution on reductive elimination. Both disfavor a phosphine dissociation preequilibrium due to unfavorable gauche interactions in their ring-open forms (*gem*-dialkyl effect), interactions which are absent in dppp. At the same time, these ligands differ in their bite angles; of this series, Et_2dppp should have the smaller bite angle due to angle compression at the central carbon atom and (CH_2)$_3$dppp should have the larger bite angle due to angle enlargement (Thorpe−Ingold effect). Thus, reductive elimination by a mechanism involving chelate ring opening and a three-coordinate intermediate should exhibit the kinetic ordering **4**,**5** < **2**. Instead, the observed kinetic ordering tracks the bite angles (**4** < **2** < **5**). While this ordering result supports a mechanism involving an intact ring, the effect of *gem*-dialkyl substitution has not been widely exploited or quantified in metal−phosphine systems.[21] Therefore, these results are offered as evidence for an intact chelate ring but do not conclusively rule out a phosphine dissociation preequilibrium.[22]

Scheme 1



Activation parameters are provided in Table 1. These data show that the reductive elimination is dominated by the $\Delta H^{\ddagger}$ term, with a small but favorable entropic contribution of 0−14 eu. Trends in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are not obvious, with the exception that substituents on the chelate ring tend to increase both parameters. An interpretation of the change in $\Delta H^{\ddagger}$ is difficult[23] but the increase in $\Delta S^{\ddagger}$ may reflect increased flexibility in the transition state of the ring-substituted systems.

The small $\Delta S^{\ddagger}$ suggests that elimination of the coupled product occurs after the transition state, and the mechanism presented in Scheme 1 is proposed to account for these results. This mechanism resembles the familiar migratory insertion of CO into metal−carbon bonds to produce acyl complexes. Considering the isoelectronic relationship between CO and CN^-, this is a reasonable conclusion. Further note that reductive elimination of (CH_3)$_3$$CCH_2CN$ is faster than $TMSCH_2CN$. Elimination of CH_3CN from (diphosphine)Pd(CH_3)(CN) is, in turn, much slower than $TMSCH_2CN$,[24] and thus the kinetic ordering with respect to the alkyl group is (CH_3)$_3$$CCH_2$ > $TMSCH_2$ ≫ CH_3. This order, as well as its magnitude, is the same as that observed for migratory CO insertion,[25] adding further support to the suggestion that the mechanisms are related.[26] These results have bearing on other examples of reductive elimination reactions in that they also appear to involve a migration mechanism involving three-center transition states and σ or π bound intermediates, as opposed to concerted mechanisms.[1b,4,8]

In conclusion, relatively minor changes in the chelate bite angle have been shown to induce a significant effect (ca. 10^4-fold) on the rate of reductive elimination. Further studies of the effect of ancillary ligands on reductive elimination reactions are in progress.

Acknowledgment. We thank Dr. E. E. Bunel, Ms. L. A. Howe, and Ms. C. Kelly for expert assistance with the kinetics measurements.

Supporting Information Available: Text describing synthetic, spectroscopic, and analytical data for the complexes (diphosphine)Pd(R)(CN), details regarding the kinetic measurements, and Eyring plots (10 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(16) This is clearly seen in the structures of diphosPdCl_2,[16a] dpppPdCl_2,[16a] and DIOPPdCl_2,[16b] where the Cl···Cl distance decreases from 3.397 Å to 3.341 Å to 3.280 Å, respectively. (a) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432. (b) Gramlich, V.; Consiglio, G. *Helv. Chim. Acta* **1979**, *62*, 1016.

(17) Evidence for an associative process in the reductive elimination of RCN from P_2Ni(R)(CN) has been presented: McKinney, R. J.; Roe, C. *J. Am. Chem. Soc.* **1986**, *108*, 5167.

(18) (a) Komiya, S.; Albright, T. A.; Hoffman, R.; Kochi, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7255. (b) Kuch, P. L.; Tobias, R. S. *J. Organomet. Chem.* **1976**, *122*, 429.

(19) This assumes that isomerization of the resulting T-shaped intermediate is rapid relative to reductive elimination. Evidence for this has been presented in the case of reductive elimination from R_3PAuR′$_3$[18a] and (R_3P)$_2$PdR′$_2$.[1d]

(20) For a good discussion of these effects, see: Jung, M.; Gervay, J. *J. Am. Chem. Soc.* **1991**, *113*, 224.

(21) Shaw has shown that bulky substituents on phosphorus drive ring-forming reactions in metal−diphosphine systems: Shaw, B. L. *Adv. Chem. Ser.* **1982**, *196*, 101.

(22) An unverified assumption built into our argument is that the energetics of the gauche interactions manifested as the *gem*-dialkyl effect are at least comparable to those driving ring opening (i.e., enlarged bite angle).

(23) Reference 2c, p 16.

(24) M. J. Burn (Du Pont), unpublished observations.

(25) Cotton, J. D.; Crisp, G. T.; Latif, L. *Inorg. Chim. Acta* **1981**, *47*, 171.

(26) CO insertion into the Pd−CH_3 bonds of (diphosphine)Pd(CH_3)Cl and (diphosphine)Pd(CH_3)L^+ is also accelerated by diphosphines with large bite angles: Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. *Organometallics* **1992**, *11*, 1598.