Table I. Reduction of Organic Substances with $NaBH_3SCN \cdot 2$(dioxane) in THF[a]

subst	molar ratio (deriv/subst)	temp	reaction time, h	product[b]
C_6H_5CN	1.5	reflux	20	$C_6H_5CH_2NH_2 \cdot HCl$ (86)
$(C_6H_5)_2CHCN$	2.0	reflux	17	$(C_6H_5)_2CHCH_2NH_2$
$C_6H_5NO_2$	2.1	reflux	20	no reduction
$C_6H_5COOCH_3$	2.8	reflux	20	no reduction
$C_6H_5CONH_2$	1.5	reflux	21	$C_6H_5CH_2NH_2 \cdot HCl$ (75)
$C_6H_5COCH_3$	1.6	ambient	6	$C_6H_5CH(OH)CH_3$ (100)
CH_3COCH_3	1.5	ambient	6	$(CH_3)_2CHOH$ (100)
C_6H_5CHO	1.5	ambient	4	$C_6H_5CH_2OH$ (100)
C_6H_5COCl	1.4	ambient	4	$C_6H_5CH_2OH$ (100)

[a] Reactions were not optimized. [b] Percent yields are in parentheses.

crystalline solid which analyzed approximately as $3NaSCN \cdot 2BH_3$ was obtained by reducing the volume of the solution. No attempt was made to further characterize this species. Anal. Calcd.: H^-, 2.23; B, 7.98; Na, 25.46. Found: H^-, 2.61; B, 7.95; Na, 23.80.

$NaBH_3SCN$ is slightly more stable hydrolytically than $NaBH_4$. Thus, in pH 5 buffer solution, only ~50% active hydride was lost in 10 min ($t_{1/2}$ = 0.035 s for $NaBH_4$). $NaBH_3CN$ is stable even in pH 3 solution.[5] This is consistent with the stronger electron-withdrawing ability of CN in comparison to SCN. Consequently, $NaBH_3SCN$ is expected to be a stronger reducing agent, and our results presented below demonstrated this point.

Sodium Cyanoborohydride

While NaCN reacted smoothly to give $NaBH_3CN$, other inorganic salts such as KI, NaOH, or NaOCN did not react with $BH_3 \cdot THF$. Therefore, $NaBH_3CN$ was made by stirring equimolar $BH_3 \cdot THF$ (~1 M) with NaCN in THF in excellent yield. Alternatively, $NaBH_4$ and $BF_3 \cdot THF$[4] were reacted in THF to generate $BH_3 \cdot THF$ in situ, followed by further reaction with NaCN in the similar manner. We found that the reaction was sluggish when $BF_3 \cdot OEt_2$ was used instead. $NaBH_3CN$, which has been prepared from $NaBH_4$ and HCN in THF,[5] often discolors after several months of storage under ambient conditions. The present synthetic route does not involve the use of HCN, and the product has much better storage stability. No discoloration was observed and the decomposition was less than 5% when a sample was stored in a capped bottle for 7 months. The properties of $NaBH_3CN$ have been well documented.[1,2]

Reduction of Organic Functional Groups

Results of reduction using $NaBH_3SCN \cdot 2$(dioxane) are presented in Table I. THF solutions of $NaBH_3SCN$ readily reduce benzoyl chloride and benzaldehyde to benzyl alcohol. Acetone and acetophenone are reduced to the respective secondary alcohols. While nitro and ester functional groups are not reduced, nitriles and amides are reduced to the corresponding amines in THF under refluxing conditions. Aldehydes and ketones are readily transformed into alcohols by $NaBH_4$ and $NaBH_3CN$ (at pH less than 7). However, under normal conditions, nitrile or amide compounds cannot be reduced by $NaBH_4$ or $NaBH_3CN$.[6] Although $LiAlH_4$ can also serve this purpose, it reduces various functional groups indiscriminately. Nitriles and amides can be reduced to the corresponding amines by $NaBH_4$ in the presence of a carboxylic acid.[7] In view of this, $NaBH_3SCN$ should be of considerable synthetic value due to its selectivity and operational simplicity.

Experimental Section

Materials. Sodium (thiocyanato)borohydride was prepared as described previously.[3] $BH_3 \cdot THF$, sodium borohydride, sodium thiocyanate, and sodium cyanide were obtained from Alfa, Ventron/Thiokol, Beverly, MA. Reagent grade nitrobenzene, benzonitrile, diphenylacetonitrile, methyl benzoate, benzamide, benzoyl chloride, acetone, acetophenone, and benzaldehyde were obtained from Aldrich Chemical Co., Milwaukee, WI. Reagent grade THF was dried over calcium hydride before use.

Preparation of Sodium Cyanoborohydride. Two moles of $BH_3 \cdot THF$ (1.0 M) was added dropwise in 1.5 h to NaCN (101.2 g, 2.06 mol) in THF (300 mL) under an N_2 atmosphere. The reaction mixture was poststirred for 4 h and then heated under flux for 7 h. When the mixture was cooled to room temperature, the small amount of unreacted NaCN was separated by filtration under an N_2 atmosphere. Evaporation of the filtrate to dryness under reduced pressure at 60 °C gave 114 g (91%) of $NaBH_3CN$.

Anal. Calcd for $NaBH_3CN$: H^-, 4.81; H, 4.81; C, 19.11; CN^-, 41.41. Found: H^-, 4.30; H, 4.64; C, 20.97; CN^-, 39.50.

Alternatively, $BF_3 \cdot THF$[4] (2.18 mol) was added to $NaBH_4$ (65.7 g, 1.74 mol) suspended in THF (810 mL) cooled in an ice bath under an N_2 atmosphere. After a postaddition stirring period of 1.5 h, NaCN (112.7 g, 2.30 mol) was added slowly in small batches. When addition was complete, the reaction mixture was stirred for 4 h at room temperature and then heated under reflux for 7 h. After cooling and filtration under N_2, the filtrate was evaporated and the residue dried in a vacuum oven to obtain 116.6 g (85%) of $NaBH_3CN$.

Reduction of Organic Substrates. THF solution (25 mL) of the organic substrate (~0.5 M) and $NaBH_3SCN \cdot 2$(dioxane) were stirred at room temperature or heated under reflux (Table I). The resulting solution was taken to dryness under reduced pressure, and the excess reagent decomposed with dilute HCl. The aqueous solution was extracted with $CHCl_3$. The $CHCl_3$ solution was then washed with water and dried over anhydrous Na_2SO_4. The product was analyzed by gas chromatography (Hewlett-Packard FM-100 Carbowax column), and the amines were isolated as hydrochlorides.[7]

Registry No. $NaBH_3CN$, 25895-60-7; $NaBH_3SCN$, 66750-84-3; $BH_3 \cdot THF$, 14044-65-6; NaCN, 143-33-9; $BF_3 \cdot THF$, 462-34-0; $NaBH_4$, 16940-66-2; C_6H_5CN, 100-47-0; $(C_6H_5)_2CHCN$, 86-29-3; $C_6H_5CONH_2$, 55-21-0; $C_6H_5COCH_3$, 98-86-2; CH_3COCH_3, 67-64-1; C_6H_5CHO, 100-52-7; C_6H_5COCl, 98-88-4; $C_6H_5CH_2NH_2 \cdot HCl$, 3287-99-8; $(C_6H_5)_2CHCH_2NH_2$, 3963-62-0; $C_6H_5CH(OH)CH_3$, 98-85-1; $(CH_3)_2CHOH$, 67-63-0; $C_6H_5CH_2OH$, 100-51-6; $NaBH_3NCS$, 74482-65-8.

(4) H. C. Brown, "Organic Syntheses via Boranes", Wiley, New York, 1975.
(5) R. C. Wade, E. A. Sullivan, J. B. Berschied, Jr., and K. F. Purcell, *Inorg. Chem.* 9, 2146 (1970).
(6) Sodium Borohydride Brochure, Ventron Division, Thiokol Corp., Jan 1979.
(7) N. Umino, T. Iwakuma, and N. Itoh, *Tetrahedron Lett.*, 2875 (1976).

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Reduction of a Coordinated Pyridine Ring in a Macrocyclic Ligand–Nickel(II) Complex

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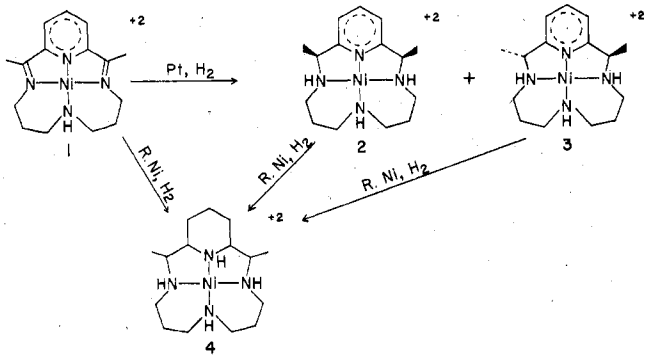
Oxidation and reduction reactions of coordinated ligands are playing an increasingly important role in the synthesis of metal complexes. This is especially true in the case of macrocyclic ligand systems where many compounds containing new ligands have been prepared by such techniques. It might be noted that macrocyclic ligand complexes are often very inert and thus can be subjected to the sometimes harsh conditions required for these reactions.

Many examples of ligand reduction have involved the conversion of coordinated imine functions to seconary amines. A

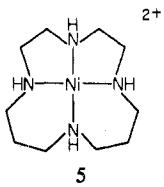
0020-1669/80/1319-3186$01.00/0

Scheme I



number of reagents have been utilized in such conversions including hydrogen with heterogeneous catalysts. Platinum and Raney nickel have been most frequently used as catalysts; but, there have been few instances where more than one catalyst has been utilized for a given hydrogenation reaction.[1]

An early example of a catalytic hydrogenation involved the conversion of **1** to a 10:1 mixture of **2** and **3** using platinum as catalyst.[2] (See Scheme I.) I find that substitution of Raney nickel for the platinum catalyst results in the formation of **4**. This note describes the properties of this compound and compares them with those of **2** and **3** and with those of **5**, which is the complex of the unsubstituted macrocyclic ligand isocyclam.[3,4]



5

Results and Discussion

The product **4** obtained from Raney-nickel-catalyzed reduction of **1** (or **2**) is yellow or orange depending on the method of crystallization, vide infra, whereas **2** is a darker red-orange. The infrared and ^{1}H NMR spectra of **4** contain no absorptions for a pyridine nucleus.[5] The NMR spectrum of the major fraction (corresponding to ≥75% isolated yield) contains a single doublet at τ 8.81 (J = 6 Hz (220 MHz, trifluoroacetic acid)) as expected for the methyl group. These data coupled with excellent analytical data (for the perchlorate salt) confirm that **4** has the indicated composition.

Inspection of **4** shows that there are four asymmetric carbon atoms, two asymmetric nitrogen atoms, and two additional nitrogen donors that are not asymmetric but which increase the number of possible isomers because of the geometric isomerism associated with them. These eight stereochemically active centers result in a total of 128 possible stereoisomers (56 pairs of optical isomers and 16 meso forms).[6] Since the hydrogenation reaction was conducted at nearly neutral pH, where proton dissociation from nitrogen could occur, only the stereochemistries of the four carbon carbon centers can be confidently assumed to be the same as those obtained from the hydrogen addition. These four asymmetric carbon atoms generate ten isomers (four pairs of optical isomers and two meso forms) that are not interconvertible through changes in nitrogen configurations. Thus, for the *free ligand* there should be six forms that are in principle distinguishable by NMR (two or these would have diastereotopic methyl groups and thus could give two resonances). Observation of a single methyl doublet for the complex indicates that the Raney-nickel-catalyzed hydrogenation is a highly stereoselective process. If, as expected, dissolution of the isolated complex into acidic solution occurs without change of nitrogen configuration[7] and the complex is stereochemically stable in solution,[7] then the observation of the single methyl doublet also reflects the greater thermodynamic stability of a particular set of nitrogen configurations compared to the several others possible for a given set of carbon configurations. Consideration of the structure of **2** and known chelate ring stabilities suggests that the most likely stereochemistry for this complex is one that has chair conformations for the six-membered chelate rings as well as for the piperidine ring and gauche conformations for the five-membered chelate rings, with substituents in equatorial positions. (See Figure 1.)

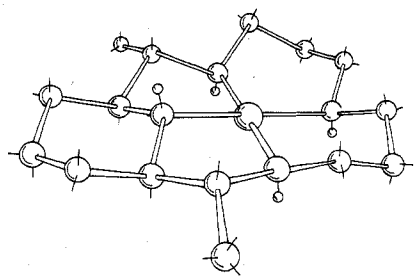


Figure 1.

Evaporation of the mother liquor after isolation of a 75% yield of **4** gave a small amount (~5%) of a solid that showed at least two methyl resonance doublets (of unequal intensity, so they could not arise from a single isomer) in addition to that of **4**. Reduction of **2** gave **4** as the only detectable product (NMR). Thus, it seems likely that reduction of **1** using Raney nickel first produces a mixture of **2** and **3** in approximately the same ratio as with platinum and that **2** is further reduced to a single product whereas **3** yields two or more products. This point was not pursued further.

When **4** was first prepared, it appeared there were two major isomers as recrystallization of the perchlorate salt from acidic ethanol–water mixtures produced yellow and/or orange crystalline compounds depending on the conditions. The two forms of **4** do not differ by inversion at a donor nitrogen as

(1) Information of this variety is not readily obtained. However, the cis and trans isomeric forms of $[Ni(Me_6[14]dieneN_4)]^{2+}$ have been reduced with use of both platinum and Raney nickel as catalysts (see: Curtis, N. F. *Coord. Chem. Rev.* **1968**, *3*, 3–47). On the other hand, nickel complexes of macrocyclic ligands containing α-diimine functions can be reduced with Raney nickel but not platinum as catalyst (Barefield, E. K. Ph.D. Thesis, The Ohio State Univeristy, 1969).

(2) Karn, J. L.; Busch, D. H. *Inorg. Chem.* **1969**, *8*, 1149–1153.

(3) Studies on the nickel complex have been reported: Sabatini, L.; Fabbrizzi, L. *Inorg. Chem.* **1979**, *18*, 438–444.

(4) This ligand and some of its metal complexes have also been reported by Blinn and co-workers: Swisher, R. G.; Smiericiak, R. S.; Blinn, E. L. "Abstracts of Papers", 175th National Meeting of the American Chemical Society, Anahiem, Calif., 1978; American Chemical Society: Washington, D.C., 1978; INOR 182.

(5) Infrared and NMR spectral data for **1** and its oxidized and reduced forms have been published: Barefield, E. K.; Lovecchio, F. V.; Tokel, N. E.; Ochiai, E.; Busch, D. H. *Inorg. Chem.* **1972**, *11*, 283–288.

(6) The six *asymmetric* centers give rise to 36 stereoisomers, of which 4 are meso and 32 are enantiomers. The additional two sites of stereoisomerism increase the number of isomers possible as follows: 4 times the number of meso forms (4 × 4 = 16); 4 times the enantiomeric forms that to do not have C_2 symmetry (24 × 4 = 96); 2 times the enantiomeric forms that have C_2 symmetry (8 × 2 = 16). Thus the total number of isomers is 96 + 16 + 16 = 128.

(7) Other nickel(II) complexes of macrocyclic tetraaamines that exhibit diastereoisomerism as a result of two or more asymmetric nitrogen donors maintain their stereochemical integrity in acidic media, and isolated isomeric forms can be redissolved without isomerization. One such complex containing two asymmetric nitrogen donors was separated into the meso and racemic forms, and the latter was resolved by adsorption on both starch and cellulose (pH <3). The enantiomers could be isolated and redissolved in acidic medium without loss of activity: Warner, L. G.; Rose, N. J.; Busch, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 703–704. Warner, L. G.; Busch, D. H. *Ibid.* **1969**, *91*, 4092–4101. Warner, L. G. PhD. Thesis, The Ohio State University, 1968.

Table I. Solution Data for 4 and Related Complexes

complex	$\tilde{\nu}$, cm^{-1}	ϵ, M^{-1} cm^{-1} [a]	proportion planar form, % (25 °C) 0.1 M Na-ClO_4	7.2 M Na-ClO_4	CH_3CN	oxidn potential [b]
4	22 470	120	100	100	34	0.81
5 [c]	21 600	116	61	100	18	0.8 [d]
2	21 000 [e]		~63 [f]		45 [c]	0.89 [g]
$[Ni(cyclam)]^{2+}$ [h]	22 470	65	71	100	22	0.67

[a] Aqueous solution; corrected where necessary to 100% planar form. [b] Vs. 0.1 M Ag^+/Ag reference electrode in CH_3CN/0.1 M n-Bu_4NBF_4 solution. [c] Data taken from ref 3. [d] Value recorded in ref 3 as 0.84 vs. 0.01 M Ag^+/Ag electrode. Comparison of other data relative to this electrode with that obtained relative to 0.1 M indicates a difference of 30–40 mV rather than the theoretical. 59. [e] Datum taken from ref 2. [f] Value was determined by magnetic susceptibility measurements on aqueous solutions—effect of added electrolyte has not been determined. [g] Datum from ref 9. [h] Data from ref 10.

shown by their identical NMR spectra in trifluoroacetic acid and their identical absorption spectra in H_2O and 0.1 M $HClO_4$ (λ_{max} = 445 nm, ϵ = 120 M^{-1} cm^{-1}).[7] The two forms show only slight differences in their infrared spectra. The orange form appears to be kinetically controlled with the yellow being thermodynamically most stable. Only the orange form can be detected (microscope) when either the orange or yellow form is crystallized from acetone by addition of ether. Solid-state spectra, obtained by the diffuse-transmittance technique, show λ_{max}^{orange} = 475 nm and λ_{max}^{yellow} = 455 nm. There are at least two possible explanations for the existence of the two forms: (1) One form has a perchlorate ion weakly coordinated, or (2) one form has a six-membered chelate ring (or possibly the piperidine ring) in a different conformation. I favor the latter possiblity, since work on complexes of *N*-(3-aminopropyl)-1,3-diaminopropane (dpt) has shown that both chair, chair and chair, skew boat forms of this triamine occur in solid-state forms of its Co(III) complexes.[8] Such conformational changes would affect the donor–acceptor orbital interactions and thus the electronic effect of the ligand on the metal. Rapid interconversion of these forms in solution would account for their identical behavior. Coordination of perchlorate ion would also affect the solid-state spectral properties and would not be expected to persist in solution. Although coordination of perchlorate ion is frequently detectable by infrared spectroscopy, diagnostic absorptions are frequently obscured when a noncoordinated perchlorate ion is also present. The nearly identical spectra of these two compounds in the region 1100–900 cm^{-1} suggest this is not the case, however.

A comparison of the solution properties of **4** with those of complexes of other 14-membered macrocyclic ligands is of some interest. Pertinent data for **2**, **5**, and $[Ni(cyclam)]^{2+}$ are given in Table I. Complex **5** exists in aqueous solution as a mixture of 4- and 6-coordinate species.[3] The equilibrium constant is highly dependent on temperature and ionic strength. In 7.2 M $NaClO_4$ only the 4-coordinate form is detectable, and the extinction coefficient is then temperature independent. $[Ni(cyclam)]^{2+}$ behaves similarly.[10] Complex **2** also exists as a mixture but it has been less extensively studied.[2] The behavior of **4** is somewhat different since only the 4-coordinate complex is detectable in water, and there is no change in the extinction coefficient of its absorption band in 2 M $NaClO_4$.[11] In acetonitrile, all four complexes exist as mixtures of 4- and 6-coordinate species. The relative amounts of the 4-coordinate forms of **4**, **5**, and $[Ni(cyclam)]^{2+}$ parallel those in water, whereas **2** is somewhat out of line, being relatively more in the 4-coordinate form in acetonitrile.

The position of the equilibrium $[Ni(macrocycle)L_2]^{2+} \rightleftarrows [Ni(macrocycle)]^{2+} + 2L$ is largely determined by the relative magnitude of the unfavorable loss in bonding interactions compared to the favorable entropy change and the favorable increase in Ni–N interactions that occur upon conversion from the high-spin, 6-coordinate (Ni–N distance 2.05–2.1 Å) to the low-spin, 4-coordinate form (Ni–N distance 1.85–1.95 Å). (Of course, there are other effects such as the entropy changes associated with spin pairing, differences in solvation, etc.) The absorption maximum of planar Ni(II) complexes has been suggested as a measure of the strength of the nickel–ligand interaction.[12] Thus, **4** whose visible absorption is at higher energy than that of **5** might be expected to favor the planar form, all other things being equal. At the same time, the energy of the visible absorption of **4** is identical with that of $[Ni(cyclam)]^{2+}$, which is only 71% in the 4-coordinate form in 0.1 M $NaClO_4$. An attractive explanation for this apparently anomalous behavior of **4** is that the rigidity imparted to the 5-membered chelate rings by the fused piperidine may oppose the lengthening of metal–donor distances that is expected for the 4-coordinate → 6-coordinate conversion. Unfortunately, this explanation is not consistent with the ordering of oxidation potentials which is **5** ≈ **4** < $[Ni(cyclam)]^{2+}$.

A final point of considerable interest is the difference in the activities of Pt and Raney nickel catalysts for reduction of the pyridine nucleus. Although Raney nickel is obviously more active than platinum for this reduction, the difference is not as great as it might first appear since the catalyst/complex ratio used was somewhat greater in the case of nickel (weight ratios of 2–4 were used in the case of Raney nickel whereas the ratio was about 0.04 for Pt). In fact, exposure of a solution of **2** to Pt and H_2 for 5 days did result in a very low conversion to **4** (<10%). These results are somewhat suprising because pyridines are more often reduced with platinum than nickel and the latter catalyst generally requires considerably more harsh conditions.[13] It is also true, however, that platinum-catalyzed reductions are usually done in acidic medium or on preformed pyridinium salts since these appear to reduce more rapidly than the free base. Whether this is actually true is a bit uncertain since the basic piperidine products poison platinum catalysts. Raney nickel is not usually used in acidic medium since it is oxidized in it. The present result might be interpreted to mean that nickel-complexed pyridines are very easily reduced, and one wonders whether dissolved nickel salts might increase the rates of Raney-nickel-catalyzed pyridine reductions.

Conclusions

These results further illustrate a number of points that have become increasingly obvious in the past few years. Foremost among these is how relatively small differences in ligand structure strongly affect the solution behavior of the nickel complex. Secondly, this provides a good example of the utility

(8) α- and β-$[Co(en)(dpt)Cl]^{2+}$ have the chair, skew boat set of conformations for the dpt ligand: Ireland, P. R.; House, D. A.; Robinson, W. T. *Inorg. Chim. Acta* **1970**, *4*, 137–141. House, D. A.; Ireland, P. R.; Maxwell, I. E.; Robinson, W. T. *Inorg. Chim. Acta* **1971**, *5*, 397–405. *mer*-$[Co(dpt)Cl_3]$ has the chair, chair set of conformations for dpt: Barefield, E. K.; Carrier, A. M.; Van DerVeer, D. G. *Inorg. Chim. Acta*, in press.

(9) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3108–3118.

(10) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Inorg. Chim. Acta* **1977**, *24*, L21–L23.

(11) The solubility of **4** is too low for measurements at higher $NaClO_4$ concentrations.

(12) Fabbrizzi, L. *Inorg. Chem.* **1977**, *16*, 2667–2668.

(13) Augustine, R. L. "Catalytic Hydrogenation"; Marcel Dekker: New York, 1965, pp 104–105.

of reactions of coordinated ligands for the production of new ligand systems with a high degree of stereoselectivity. This selectivity is a result of conformational and substituent orientation effects of the chelate rings.

So far as I am aware this is the only example of a macrocyclic ligand that incorporates a piperidine ring. A recent review lists literally dozens of macrocyclic compounds that contain pyridine moieties as subunits.[14] Many of these compounds were developed as metal-complexing agents. A large number of new ligands could be prepared by reduction of the pyridine subunits. If these reductions can be performed on the metal complexes, a higher degree of stereoselectivity may be expected.

Experimental Section

Complexes **1** and **2** were prepared according to the literature procedures.[2]

Raney-Nickel-Catalyzed Reductions. Reductions were done on ca. 2.5 g of **1** or **2** in 200 mL of water. Two to five grams of Raney nickel (W-2 or Grace Grade 28) was added and the mixture placed under 50 psi H_2 (Parr apparatus) and agitated until gas uptake ceased (3–5 h). After removal of the catalyst, solutions were acidified with a few drops of concentrated $HClO_4$ and evaporated to small volumes (~10 mL). The yellow-orange products that crystallized were collected and dried in vacuo. Yields were in the range 60–85%. Recrystallization of the product from **1** or **2** from acidified ethanol–water mixtures gave yellow and/or orange crystals. In one instance, orange crystals grew initially but slowly disappeared to be replaced by yellow. The yellow form could be separated from the orange by preferential dissolution of the latter in acetone. Crystallization of either form from acetone by addition of ether gave only the orange material. Anal. Calcd for $NiC_{15}H_{32}N_4Cl_2O_8$: C, 34.25; H, 6.13; N, 10.65. Found (yellow form): C, 34.27; H, 6.12; N, 10.94. Found (orange form): C, 34.31; H, 6.11; N, 10.93.

Visible spectra of **4** were determined on 10^{-3} M solutions in 5-cm cells with the use of a Cary 14 spectrophotometer or 1-cm cells with the use of a Beckman Acta V. NMR spectra were obtained at 100 and 220 MHz on trifluoroacetic acid solutions. The oxidation potential of **4** was determined by cyclic voltammetry using a standard three-electrode cell and a spherical platinum working electrode. Measurements were made on 10^{-3} M CH_3CN/0.1 M n-Bu_4NBF_4 solutions and potentials measured relative to a 0.1 M Ag^+/Ag reference electrode. At a 200 mV/s scan rate the peak current ratio was unity and the peak separation was 80 mV.

Registry No. **1**, 35270-39-4; **2**, 26149-43-9; **4**, 74185-30-1.

(14) Newkome, G. R.; Sauer, J. D.; Roper, J. M.; Hager, D. C. *Chem. Rev.* **1977**, *77*, 513–597.

Contribution from the Institut de Recherches sur la Catalyse, 69626 Villeurbanne Cédex, France

Cationic η^3-Allyl Complexes. 6. New General Synthesis of Cationic (η^3-Allyl)palladium Complexes

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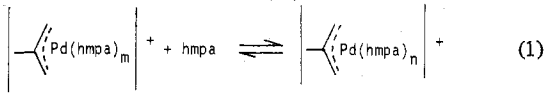
Received March 27, 1980

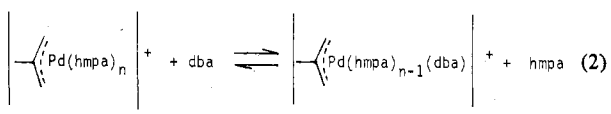
D.N.[1,2] has recently reported that (allyloxy)phosphonium (**1**) and (allylthio)uronium (**2**) salts react readily with zerovalent nickel compounds like nickel carbonyl and bis(1,5-cyclooctadiene)nickel to lead to cationic allylnickel complexes. The corresponding palladium complexes $[Pd(all)L_2]^+$ have been already reported for L = R_3P, R_3As, and coordinating solvents and L_2 = dienes, hexamethylbenzene, etc....[3] These syntheses generally require the use of silver[3b,d,e] and thallium salts[3c] of so-called noncomplexing anions or sodium tetraphenylborate.[3a] We report here an extension of the general procedure used for nickel which uses easily accessible zerovalent palladium compounds, i.e., tris(dibenzylideneacetone)dipalladium, $Pd_2(dba)_3$ (**3**),[4] or bis(dibenzylideneacetone)palladium (**4**),[5] and allylic salts[6,7] together with preliminary observations on the mechanism of the formation of these complexes.

As stated by Ishii and his co-workers,[8] $Pd_2(dba)_3$ reacts smoothly with allyl halides to give allylchloropalladium(II) complexes. Reaction of equimolar amounts of **1a** with **3** in dichloromethane was monitored by UV–vis spectroscopy (10^{-4} M solution). After 2 h, the absorption at 524 nm we assigned to coordinated dba vanished and a stable, yellow solution containing free dba was obtained. ^1H NMR spectroscopy (CH_2Cl_2, 10^{-1} M) shows the presence of a 2-methallyl ligand (δ 2.29, s, 2-methyl; δ 2.98, s, anti H; δ 3.93, s, syn H, assuming the resonance of CH_2Cl_2 at 5.35 ppm) together with the signals awaited for hexamethylphosphorotriamide, hmpa (δ = 2.66, ^3J(H–P) = 9.5 Hz) and dibenzylideneacetone (δ = 7–8). Proton-decoupled ^{31}P NMR spectroscopy indicates the coordination of hmpa to the Pd(II) ion (δ = +36 for the salt **1a**, δ = +30.4 for the solution of complex **5**, δ = 24.1 for free hmpa, in CH_2Cl_2). Addition of increments of hmpa indicate a monotonic shift of the ^{31}P signals toward the position observed for a solution of hmpa in CH_2Cl_2 (i.e., 1 equiv of hmpa, δ = 29.4; 3 equiv of hmpa, δ = 27.0; 9 equiv of hmpa, δ = 25.2), suggesting the occurrence of the exchange



(1)

Futhermore, the syn and anti protons of the 2-methylallyl ligand are also affected by the addition of hmpa. Thus, addition of 1 equiv of hmpa shifts the H_{syn} and H_{anti} signals to 3.67 and 2.67 ppm. Noteworthy is that complex **6a** (vide infra) shows H_{syn} and H_{anti} resonances at 3.87 and 2.98 ppm and a ^{31}P resonance at 30.0 ppm, values which are not very different from those observed in the reaction medium containing the evolved dba. Addition of 1 equiv of hmpa to this complex also affects these signals (respectively δ = 3.63 and 2.67). Finally, addition of free dba shifts the position of the same signals, but addition of more than 1 equiv does not further modify their positions (respectively 3.83 and 2.86 ppm). Interestingly, in this case, the vinyl protons of dba are simultaneously *deshielded* by 0.2 ppm with respect to the free ligand and by 1.15 and 2.35 ppm with respect to the coordinated ligands of $Pd_2(dba)_3$.[9] This behavior could be interpreted by the coordination to Pd(II) of the oxygen atom of the carbonyl ligand. Thus another exchange



(2)

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