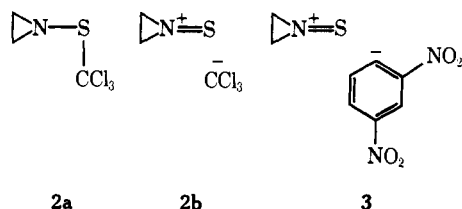


Since congestion is greater in the pyramidal ground state than in the planar transition state for nitrogen inversion, aziridines with bulky ligands at nitrogen invert more rapidly, *caeteris paribus*, than those with less bulky substituents. Thus, the barriers to inversion in *N-tert-butyl-* (17.6 kcal/mol) and *N-tert-butanesulfonyl-* (12.2 kcal/mol) aziridines are substantially lower than those in their *N-methyl* (22.3 kcal/mol) and *N-methanesulfonyl* (13.3 kcal/mol) analogs.

Bystrov, *et al.*, suggested that overlap between the nitrogen lone-pair orbital and the C–O antibonding  $\sigma$  orbital (negative hyperconjugation) is responsible for the lower barriers in *N-hydroxymethyl-* and *N-methoxymethylaziridines* in comparison to those in *N-alkylaziridines*.<sup>4</sup> Similarly, nitrogen inversion is considerably more rapid in *N-methoxymethylisoxazolidine* than can be accounted for by steric considerations,<sup>5</sup> although changes in vicinal electron-pair repulsion might offer an alternate explanation in the isoxazolidine system.<sup>6</sup> The low barriers observed in some fluorine-substituted aziridines may also be evidence of this phenomenon.<sup>7</sup>

Bystrov, *et al.*, express  $\sigma$ – $\pi$  hyperconjugation in aziridines by invoking a contribution from ( $n$ – $\sigma^*$ )  $\pi$  overlap. The same phenomenon can be viewed in a resonance framework by reference to canonical structures **2a** and **2b**. In either representation the inability



of the also highly electronegative 2,4-dinitrophenyl group to effect a rate acceleration comparable to that of the trichloromethyl group is understandable. Resonance stabilization of the carbanion orbital in **3** by the nitro groups is not possible since the  $\sigma$  bond (as well as the axis of the  $\sigma^*$  orbital) lies in the nodal plane of the aromatic  $\pi$  system.

We have prepared compounds **1a** and **1b** and examined their barriers to topomerization by measuring the temperatures for coalescence of the methylene singlets. The chemical-shift differences, coalescence temperatures, and free energies of activation were: **1a**,  $\Delta\nu = 30.5$  Hz,  $T_c = -86^\circ$ ,  $\Delta G_c^\ddagger = 9.2$  kcal/mol; **1b**,  $\Delta\nu = 35$  Hz,  $T_c = -61^\circ$ ,  $\Delta G_c^\ddagger = 10.4$  kcal/mol. Geminal coupling is small enough that line broadening is negligible in comparison to the chemical-shift difference and the expression  $k_c = \pi\sqrt{2}\Delta\nu$  provides an accurate measure of the coalescence rate.

(4) For discussions of  $\sigma$ – $\pi$  conjugation and its effects on barriers to nitrogen inversion see: (a) ref 3, footnotes 1a,b,d; (b) R. D. Bach and P. A. Scherr, *J. Amer. Chem. Soc.*, **94**, 220 (1972); (c) R. D. Baechler and K. Mislow, *Chem. Commun.*, 185 (1972); (d) J. Bystrov, R. G. Kostyanovskii, O. A. Panshin, A. U. Stepanyants, and O. A. Yuzhakova, *Opt. Spectrosc. (USSR)*, **19**, 122 (1965); *Opt. Spektrosk.*, **19**, 217 (1965).

(5) (a) F. G. Riddell, J. M. Lehn, and J. Wagner, *Chem. Commun.*, 1403 (1968); (b) D. L. Griffith and B. L. Olson, *ibid.*, 1682 (1968); (c) M. Raban, F. B. Jones, E. H. Carlson, E. Banucci, and N. A. LeBel, *J. Org. Chem.*, **35**, 1496 (1970).

(6) S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B*, 136 (1971).

(7) (a) J. B. Lambert, *Top. Stereochem.*, **6**, 19 (1971); (b) J. M. Lehn, *Fortsch. Chem. Forsch.*, **15**, 311 (1970); (c) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 401 (1970).

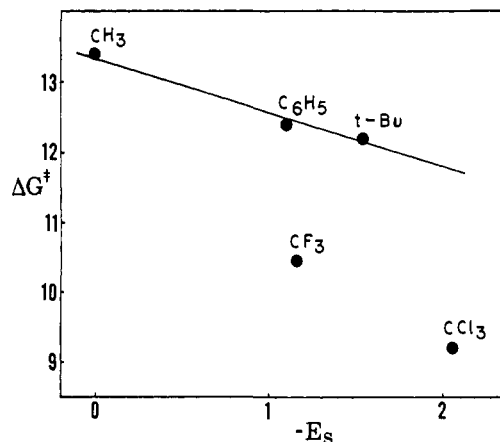


Figure 1. Plot of free energies of activation in sulfenylaziridines as a function of Taft's steric parameter,  $E_s$ .

These barriers are not in accord with an explanation based on steric factors alone. A plot of free energies of activation as a function of  $E_s$ ,<sup>8</sup> a steric parameter (Figure 1) for **1a**, **1b**, and the comparable methanesulfonyl, benzenesulfonyl, and *tert*-butanesulfonyl compounds,<sup>1a,9</sup> indicates considerable deviations for **1a** and **1b**. Both compounds have energies of activation which are *ca.* 2–2.5 kcal/mol lower than those which would be predicted on steric grounds alone. Use of  $A$  values provides a similar estimate. On the basis of the  $A$  values given for methyl, phenyl, and trifluoromethyl,<sup>10</sup> the free energy of activation for **1b** deviates by about 2.5 kcal/mol from the line formed by the other two points. Although these calculations are admittedly crude, we may be confident in concluding that steric effects cannot account for the low barriers in **1a** and **1b**. Although estimates of the size of the  $CF_3$  group vary (it is substantially larger than isopropyl on the  $E_s$  scale but slightly smaller than isopropyl on the  $A$ -value scale), under no circumstances would we imagine the trifluoromethyl group to be very significantly larger than *tert*-butyl as it would have to be if steric effects alone were responsible for the magnitude of nitrogen inversion barriers in sulfenylaziridines. By exclusion, then, our data suggest that negative hyperconjugation stabilizes the inversion transition state in **1a** and **1b** by about 2–3 kcal/mol.<sup>11</sup>

(8) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

(9) A value of 1.1 was estimated for  $E_s(C_6H_5)$  since this value is about 40% larger than that for  $E_s(C_6H_{11})$  and the  $A$  value for phenyl is 40% larger than that for cyclohexyl.<sup>10</sup>

(10) J. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

(11) We thank Professor J. M. Lehn for a helpful discussion. This work was supported by the National Science Foundation and the U. S. Public Health Service.

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## Preparation and Identification of CO and N<sub>2</sub> Complexes of NiF<sub>2</sub> and NiCl<sub>2</sub> by Matrix Isolation

Sir:

Although palladium(II) and platinum(II) carbonyl halides exist, no carbonyl halides of nickel(II) are

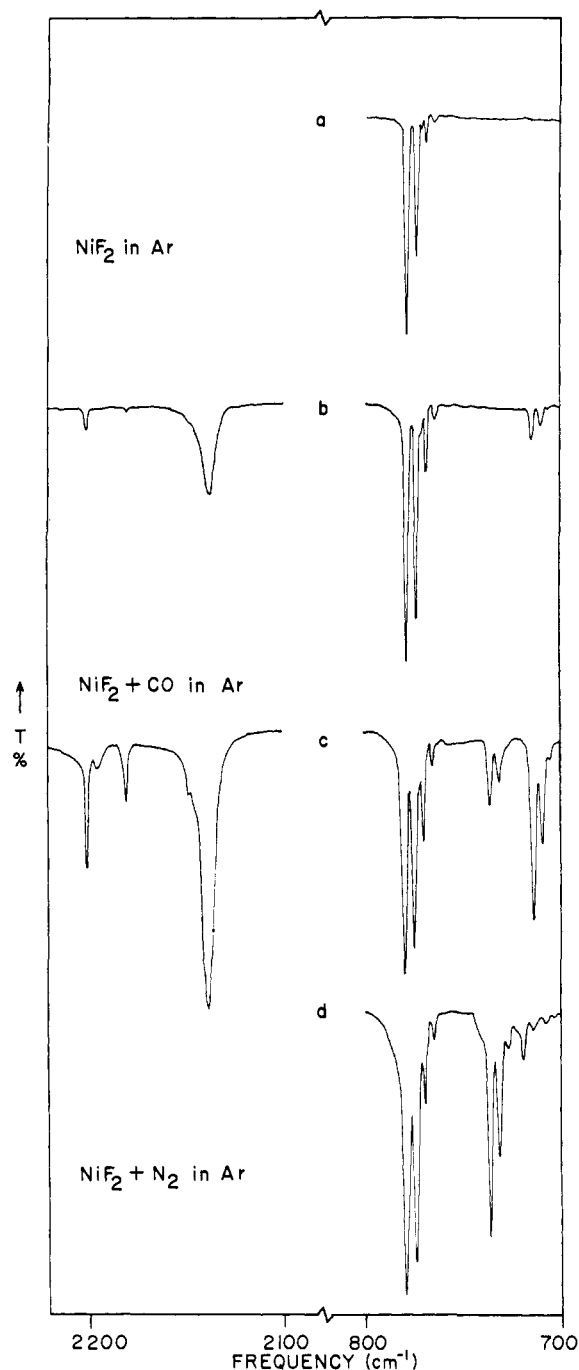


Figure 1.  $\text{NiF}_2$  isolated in argon matrices doped with CO or  $\text{N}_2$ .

known. In this communication we wish to report the preparation and identification of both CO and  $\text{N}_2$  complexes of  $\text{NiF}_2$  and  $\text{NiCl}_2$  using the matrix isolation method.

The infrared spectra of  $\text{NiF}_2$  and  $\text{NiCl}_2$  isolated in argon matrices have been extensively studied.<sup>1</sup> Nearly all these investigators noted additional transitions (e.g., at 735 and 713  $\text{cm}^{-1}$  for  $\text{NiF}_2$  and at 483 and 463  $\text{cm}^{-1}$  for  $\text{NiCl}_2$ ) which could not be assigned. These "impurity transitions" were found to be particularly

(1) (a) D. E. Milligan, M. E. Jacox, and J. D. McKinley, *J. Chem. Phys.*, **42**, 902 (1965); (b) K. R. Thompson and K. D. Carlson, *ibid.*, **49**, 4379 (1968); (c) J. W. Hastie, R. H. Hauge, and J. C. Margrave, *High Temp. Sci.*, **1**, 76 (1969); (d) M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, **51**, 4143 (1969); (e) J. W. Hastie, R. H. Hauge, and J. L. Margrave, *High Temp. Sci.*, **3**, 257 (1971).

intense when depositions were carried out at high Knudsen cell temperatures and when a leak was known to be present in the vacuum system.<sup>1a</sup> These transitions may now be assigned to  $\text{NiF}_2\text{N}_2$ ,  $\text{NiF}_2\text{CO}$ ,  $\text{NiCl}_2\text{N}_2$ , and  $\text{NiCl}_2\text{CO}$ .

The matrix isolation technique used in this study is well known and our experimental apparatus is described elsewhere.<sup>2</sup> The argon was doped with CO or  $\text{N}_2$  using a very low flow-rate valve together with a tee in the argon line or by passing the CO or  $\text{N}_2$  directly into the furnace chamber. Doping concentrations of either CO or  $\text{N}_2$  in argon were as low as 1/500 to as high as 1/50 depending on the experiment. The  $\text{NiF}_2$  and  $\text{NiCl}_2$  were dehydrated prior to use and vaporized from a nickel Knudsen cell.

The spectrum of pure  $\text{NiF}_2$  from a well-outgassed nickel Knudsen cell and well-outgassed furnace chamber is shown in Figure 1a. No absorptions other than those between 765 and 780  $\text{cm}^{-1}$  are observed. These may readily be assigned to  $\nu_3$  of  $\text{NiF}_2$  with the individual absorptions due to the various nickel isotopes.

Figure 1b shows the spectrum of  $\text{NiF}_2$  in argon doped with CO. An absorption at 713  $\text{cm}^{-1}$  appears together with a transition at 2200  $\text{cm}^{-1}$  and the usual CO absorption at 2138  $\text{cm}^{-1}$ . Figure 1c shows the same system but with a more concentrated matrix of  $\text{NiF}_2$  and CO. Figure 1c clearly shows the strong similarity between the 713- and 780- $\text{cm}^{-1}$  absorptions. The additional transition at 2179  $\text{cm}^{-1}$  observed in Figure 1c is assigned to an  $(\text{NiF}_2)_2\text{CO}$  complex to be reported in a forthcoming publication. Addition of  $^{13}\text{CO}$  shifts the 2200- $\text{cm}^{-1}$  transition to 2151  $\text{cm}^{-1}$  and addition of 50%  $^{12}\text{CO}$  and 50%  $^{13}\text{CO}$  mixture gives no new CO frequencies between 2200 and 2150  $\text{cm}^{-1}$  proving that only one CO is attached to the  $\text{NiF}_2$ . We then assign the 2200- $\text{cm}^{-1}$  transition to the C-O stretch and the 713- $\text{cm}^{-1}$  transition to an asymmetric F-Ni-F stretch of an  $\text{NiF}_2\text{CO}$  complex. An excellent fit is obtained for the 713- $\text{cm}^{-1}$  transition using the isotope relation for the asymmetric stretch of free  $\text{NiF}_2$  with a 150° bond angle. This calculation is equivalent to assuming that the normal modes of the same symmetry as the F-Ni-F asymmetric stretch of an  $\text{NiF}_2\text{CO}$  complex do not perturb the isotopic splitting of the F-Ni-F asymmetric stretch.

The spectrum of  $\text{NiF}_2$  isolated in argon doped with  $\text{N}_2$  is shown in Figure 1d. A 736- $\text{cm}^{-1}$  absorption now grows in very strongly which is assigned to an F-Ni-F asymmetric stretch of an  $\text{NiF}_2\text{N}_2$  complex.

Turning now to  $\text{NiCl}_2$ , the same behavior is observed when CO or  $\text{N}_2$  is added to the argon matrix. The spectrum of pure  $\text{NiCl}_2$  from a well-outgassed nickel Knudsen cell and furnace chamber is identical with that previously reported except now the 483- and 468- $\text{cm}^{-1}$  transitions are absent. Addition of CO to the argon results in new transitions at 468  $\text{cm}^{-1}$  and in the CO stretching region at 2189 and 2153  $\text{cm}^{-1}$ . In addition, the usual CO absorptions observed by Pimentel, *et al.*,<sup>3</sup> at 2148, 2144, and 2138  $\text{cm}^{-1}$  are seen. The absorption at 2153  $\text{cm}^{-1}$  is due to free CO in a new matrix site. It occurs only when the CO has come in contact with the hot Knudsen cell and is absent when the CO is brought in through the argon tee.

(2) R. D. Wesley and C. W. DeKock, *J. Chem. Phys.*, **55**, 3866 (1971).

(3) G. E. Leroi, G. E. Ewing, and G. C. Pimentel, *ibid.*, **40**, 2298 (1964).

Upon addition of  $^{13}\text{CO}$  the  $2189\text{-cm}^{-1}$  absorption shifts to  $2140\text{ cm}^{-1}$ . No intermediate absorptions are observed when  $\sim 50\%$   $^{12}\text{CO}$  and  $\sim 50\%$   $^{13}\text{CO}$  are added. The strong similarity between the  $468\text{-cm}^{-1}$  and  $520\text{-cm}^{-1}$  transitions suggests that the  $468\text{-cm}^{-1}$  absorption is due to a Cl-Ni-Cl asymmetric stretch of an  $\text{NiCl}_2\text{CO}$  complex. Addition of  $\text{N}_2$  to the argon results in a new absorption at  $483\text{ cm}^{-1}$ . This is assigned to an  $\text{NiCl}_2\text{N}_2$  complex. Both of these transitions can be fit very well using the isotope relation for free  $\text{NiCl}_2$  assuming a  $180^\circ$  Cl-Ni-Cl bond angle.

The frequency of the C-O stretch in these complexes is of interest since to our knowledge no other metal carbonyls exhibit stretching frequencies as high as observed here. It is well known that the C-O frequency increases upon metal-carbon  $\sigma$ -bond formation while M-CO  $\pi$  bonding reduces the C-O frequency.<sup>4</sup> We suggest that the  $\text{NiX}_2\text{CO}$  complexes may best be thought of as entirely  $\sigma$ -bonded systems.<sup>5</sup>

Less can be said about the nitrogen complex since the N-N stretch is unobserved. The nickel and chlorine isotopic structure for  $\text{NiF}_2$  and  $\text{NiCl}_2$  again supports little or no change in the X-Ni-X bond angle upon complex formation. In fact, Margrave, *et al.*,<sup>1e</sup> found that the  $483\text{-cm}^{-1}$  absorption for  $\text{NiCl}_2$  could be fit very well assuming a  $180^\circ$  angle for  $\text{NiCl}_2$ . They, however, interpreted the  $483\text{-cm}^{-1}$  absorption as  $\text{NiCl}_2$  present in a different site. Although it is difficult to argue that this is not the case, yet it would appear from the definite  $\text{NiX}_2\text{CO}$  complex formation that a weakly bound nitrogen complex is forming.

**Acknowledgments.** We wish to thank the U. S. Atomic Energy Commission for support of this research and the National Science Foundation for an equipment grant for the purchase of the Perkin-Elmer 180 infrared spectrometer.

(4) L. H. Jones, *J. Mol. Spectrosc.*, **9**, 130 (1962).

(5) See, for example, the discussion on  $\sigma$ -bonded complexes in T. C. Brown and D. J. Darensbourg, *Inorg. Chem.*, **6**, 971 (1967).

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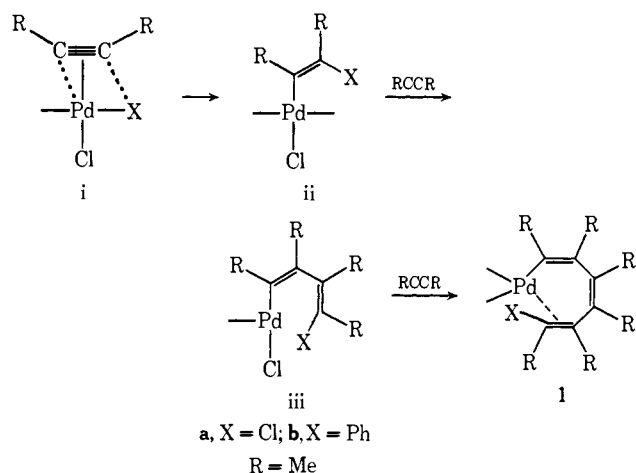
Received January 7, 1972

**Structure of  $\text{C}_5\text{Me}_5\text{CH}(p\text{-tolyl})\text{CH}_2\text{Pd}(\text{acac})$ , a  $\sigma, \pi$ -Organopalladium Complex, from the Trimerization of 2-Butyne with Tolylpalladium Chloride. A Dihaptocyclopentadiene**

Sir:

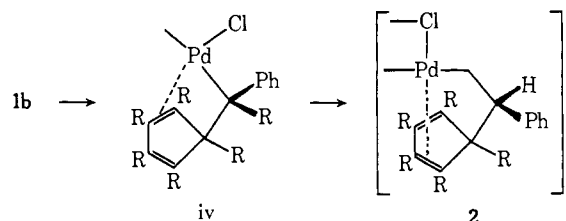
We recently described the reaction of 2-butyne with  $\text{PdCl}_2$  to give a complex  $[\text{Cl}(\text{C}_2\text{Me}_2)_3\text{PdCl}]_2$  (**1a**).<sup>1</sup> In our analysis of the reaction we suggested that it proceeded by initial coordination of one molecule of 2-butyne to  $\text{PdCl}_2$  (**ia**) followed by a relatively slow (rate-determining) cis insertion of the acetylene into a Pd-Cl bond to give a  $\sigma$ -vinyl intermediate **iiia**. This can then react by a series of fast cis-insertion reactions (*via* **iiia**) with more butyne to build up a helical chain until the reaction stops (for steric reasons), largely at **1a**.

(1) (a) H. Dietl, H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **92**, 2276 (1970); (b) H. Reinheimer, J. Moffat, and P. M. Maitlis, *ibid.*, **92**, 2285 (1970); (c) P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. II, Academic Press, New York, N. Y., 1971, pp 51-57.

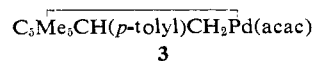


If this proposal is correct then it should be even easier to carry out this reaction with "phenylpalladium chloride"<sup>2</sup> since insertion generally occurs more easily into a Pd-C than into a Pd-Cl bond. We have treated 2-butyne with diphenylmercury and bis(benzonitrile)-palladium chloride (molar ratio 7:1:1) in either benzene or dichloromethane at  $20^\circ$  and have obtained in 45% yield a crystalline complex **2**,<sup>4</sup> stoichiometrically analogous to **1a** (Ph in place of one Cl), but with a totally different type of  $^1\text{H}$  nmr spectrum. In  $\text{CDCl}_3$  and other noncoordinating solvents the spectrum is very complex owing to an exchange process; this, however, does not occur in  $\text{CDCl}_3\text{-DMSO-}d_6$  (1:2) where clearly resolved resonances at  $\delta$  0.82 (s, 3 H), 1.48 (s, 3 H), 1.82 (s, 6 H), 1.91 (s, 3 H) 2.15 (bd m, *ca.* 2 H), 2.40 (bd m, *ca.* 1 H), and 7.28 and 7.96 (bd m, 5 H, aromatic) are observed. The complex **2** can be recovered unchanged from the solution.

On the basis of this spectrum, the analysis, and molecular weight, we proposed the structure shown for **2**; we further suggest that it arises by the reaction sequence indicated from **1b** (formed *via* **ib**, **iib**, and **iiib**) in which cyclization first occurs to give **iv**. Models show that a  $\sigma, \pi$ -bonded structure is highly strained for **iv** and it is not surprising that it undergoes a 1,2-hydride shift to give **2**.



In order to confirm the proposed structure we have carried out an X-ray determination. Unfortunately, crystals of **2** were not suitable for X-ray analysis, but the closely related acetylacetonate



(2) A phenylpalladium species, which we have arbitrarily designated as "PhPdCl," is formed *in situ* from reaction of  $\text{PdCl}_2$  and  $\text{Ph}_2\text{Hg}$ .<sup>3</sup>

(3) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968), and following papers.

(4) No **1a** and only a trace of hexamethylbenzene were formed in this reaction; however, a tetrameric complex of empirical formula  $[\text{Ph}(\text{C}_2\text{Me}_2)_3\text{PdCl}]_4$  was also isolated in 4% yield.