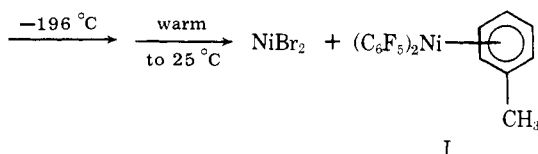


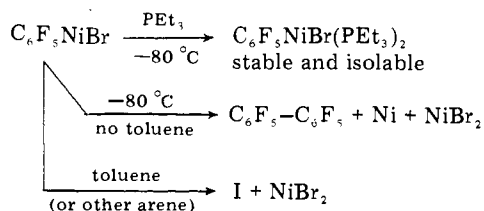
π -Arene Complexes of Nickel(II) Stabilized by σ -Bonded Pentafluorophenyl Ligands. Homogeneous Arene Hydrogenation Catalysis and Unusually Labile π -Arene Ligands

Sir:

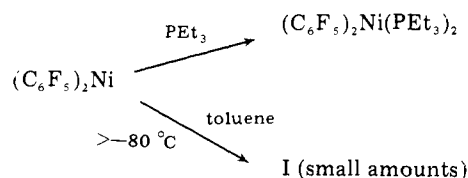
Recently we reported the synthesis and x-ray structure of a cobalt(II)- π -arene complex (η^6 -toluenebis(pentafluorophenyl)cobalt(II)).¹ We report here the synthesis and some chemistry of an analogous nickel(II) system (η^6 -toluenebis(pentafluorophenyl)nickel(II)) which is isostructural with the cobalt compound (by single-crystal x-ray analysis). The deposition of bromopentafluorobenzene, toluene, and nickel vapor together in a very simple metal vapor reactor^{1,2} efficiently yields NiBr₂ and the aforementioned complex, which can be prepared in pure 3-4-g quantities in 2 h time. An in-



termediate in this reaction sequence is C₆F₅NiBr which is stable to approximately -80 °C and can be trapped by addition of PEt₃. In the absence of a stabilizing arene ligand, C₆F₅NiBr decomposed above -80 °C to slowly yield decafluorobiphenyl,



nickel, and nickel dibromide. Bis(pentafluorophenyl)nickel may be an intermediate enroute to final products as small amounts of (C₆F₅)₂Ni can be trapped at temperatures > -80 °C by addition of PEt₃ or toluene.

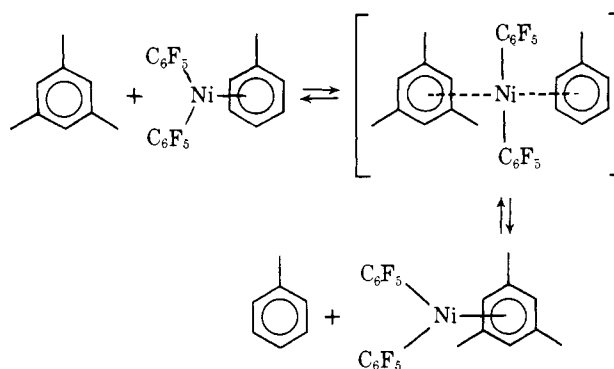


The complex I is an air-sensitive red-orange crystalline solid very soluble and stable in arene solvents. It is somewhat soluble in alkane solvents but very sensitive to decomposition in such media. It also is soluble in chloroform but with slow decomposition (several hours) yielding nickel and nickel halide precipitates. The arene ligand is exceedingly labile and can be replaced by many coordinating ligands. In fact, it is so labile that the toluene ligand can be rapidly exchanged with other arene ligands at room temperature. Analogous benzene, xylene, and mesitylene complexes can be prepared by exhaustive exchange with toluene *or* by carrying out the original metal vapor deposition procedure with bromopentafluorobenzene plus benzene, xylene, or mesitylene. Preliminary studies employing various other arenes such as fluorobenzene and anisole indicate that complexes like I are wide in scope with regard to the arene ligand that can be tolerated.

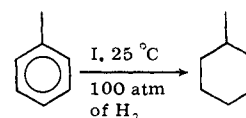
The extreme lability of the π -arene ligand allows complex I to have a rich chemistry. As detected by NMR, I is ~10% dissociated at room temperature in a 0.2 M deuteriochloroform

solution, which illustrates the ease with which reactive open coordination sites can be generated! Obviously there is an equilibrium set up between dissociated and associated toluene in chloroform, with the chloroform serving as a weak ligand.

To elucidate some of the chemistry of I we have carried out three studies. (1) Arene competition studies were investigated by adding equimolar amounts of various arenes to I in deuteriochloroform. A coordination preference of mesitylene ~ anisole > toluene > benzene > fluorobenzene > trifluoromethylbenzene was found, clearly showing that more electron-rich arenes serve as better ligands for this unusual organometallic structure. (2) Kinetic analyses at various temperatures of the π -toluene \rightarrow π -mesitylene and π -mesitylene \rightarrow π -toluene exchange were carried out. Activation energies of the order of 10-11 kcal were found (by Arrhenius methods) and the exchange in either direction was found to be first order in complex and first order in displacing arene. This indicates a transition state for exchange involving *both* the incoming arene and complex and a symmetrical intermediate (almost "S_N2 like") is possible. (3) I was studied as a homogeneous



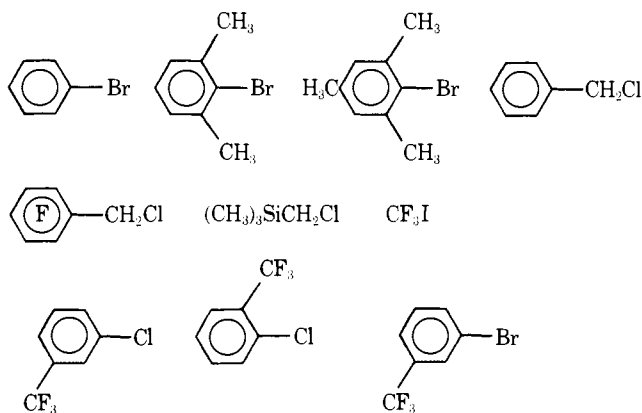
hydrogenation catalyst for arenes at room temperature.³ In toluene solution at 100 atm of hydrogen pressure, I converts toluene to methylcyclohexane at 25 °C. However, the catalyst turns over only 10 times (maximum) before it is destroyed through the hydrogenolysis of the Ni-C σ bond to yield C₆F₅H and nickel metal residue. Competition experiments between benzene and toluene indicated a slightly greater hydrogenation rate for benzene. Although it is always difficult to prove ho-



mogeneity in such systems, we believe this process is homogeneous since we tried several ways of producing active nickel powder catalysts,^{4,5} none of which served as catalysts under these conditions, which leads us to assume the nickel residue or intermediate powder formed as I decomposes is not an active catalyst (under these conditions).

Attempts to form stable complexes like I where the C₆F₅ group was replaced with other similar σ -bonded ligands have not been successful. Thus, the halides shown in Chart I were simultaneously deposited with toluene and nickel vapor, and no stable organometallics were found. For most of these halides we know reactions take place and products are formed, but the products do not have sufficient stability to be readily isolated. Therefore, the C₆F₅ group may be unique in its stabilizing effects. From an x-ray crystal study we have determined that the Ni-C σ bond in I is 1.891 (4) Å, a very short and therefore strong bond compared with other similar bond lengths in the literature.⁶ Currently we are carrying out more detailed bonding analyses which will be the subject of later publica-

Chart I



tions.⁷ At this time, in view of the electronegativity of C_6F_5 and the higher stabilities of the complexes when more electron-rich π -arenes are employed, the stabilization of the complex is a delicate balance of "push-pull" electronic configuration. This delicate stabilizing "balancing act" is needed in spite of the fact that **1** is a closed shell diamagnetic 18-electron configuration. Thus, strongly electronegative σ -bonded ligands with supposedly strong π -acceptor characteristics are required, and another good candidate is the pentachlorophenyl group, in light of the recent work of Wada and coworkers.⁸

The preparative details for synthesizing **1** are very similar to those previously described for the analogous Co complex.¹ Vaporizing 1.5 g of Ni and depositing with 50 mL of C_6F_5Br and 15 mL of dry toluene yields ~3.5 g of product crystallized from toluene: mp 137–140 °C (darkens at 125 °C); IR (KBr pellet, cm^{-1}) 3120 (w), 2940 (w), 1640 (w), 1615 (w), 1535 (m, sh), 1505 (vs), 1470 (vs), 1440 (vs, sh), 1390 (m), 1360 (m), 1280 (w, sh), 1260 (w), 1215 (w), 1180 (w), 1120 (w), 1060 (s), 1040 (m, sh), 1005 (w), 985 (w), 960 (vs), 875 (w), 800 (s), 790 (s), 730 (w). Anal. Calcd for $\eta^6-C_6H_5CH_3(C_6F_5)_2Ni$: C, 47.06; H, 1.66; F, 39.17. Found: C, 47.10; H, 1.70; F, 39.20.

Additional chemistry, x-ray structures, and syntheses of other metal(II)-arene complexes (both by metal vapor means and conventional means) will be reported soon.

Acknowledgments. Generous support of the National Science Foundation (CHE-7402713) and Research Corporation (to Lewis J. Radonovich) is acknowledged with gratitude.

References and Notes

- B. B. Anderson, C. Behrens, L. J. Radonovich, and K. J. Klabunde, *J. Am. Chem. Soc.*, **98**, 5390 (1976).
- K. J. Klabunde, *Angew. Chem., Int. Ed. Engl.*, **14**, 287 (1975); also P. S. Skell, *ibid.*, **14**, 195 (1975); P. S. Skell, L. D. Wescott, Jr., J. P. Goldstein, and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 2829 (1965); P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, **14**, 121 (1972); K. J. Klabunde, *Acc. Chem. Res.*, **8**, 393 (1975); M. Moskovits and G. Ozin, Ed., "Cryochemistry", Wiley-Interscience, New York, N.Y., 1976.
- Cf. F. J. Hirsekorn, M. C. Rakowski, and E. L. Muetterties, *J. Am. Chem. Soc.*, **97**, 237 (1975); E. L. Muetterties and F. J. Hirsekorn, *ibid.*, **96**, 4063 (1974), and references therein.
- K. J. Klabunde, H. F. Efner, T. O. Murdock, and R. Ropple, *J. Am. Chem. Soc.*, **98**, 1021 (1976).
- K. J. Klabunde, S. C. Davis, H. Hattori, and Y. Tanaka, *J. Catal.*, submitted for publication.
- Cf. M. L. Churchill and M. V. Veidis, *Chem. Commun.*, 1099 (1970).
- L. J. Radonovich, F. Koch, M. Bader, B. B. Anderson, and K. J. Klabunde, unpublished work.
- M. Wada and K. Oguro, *Inorg. Chem.*, **15**, 2346 (1976); M. Wada, Kusabe, and K. Oguro, *ibid.*, **16**, 446 (1977).

Kenneth J. Klabunde,* Bruce B. Anderson
Michael Bader, Lewis J. Radonovich*

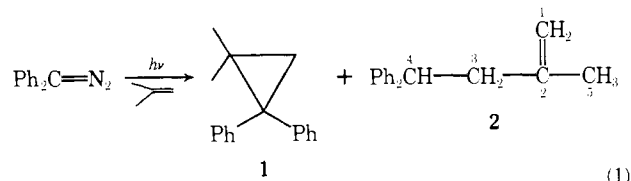
Department of Chemistry, University of North Dakota
Grand Forks, North Dakota 58201

Received October 21, 1977

Reactions of Carbenes at Low Temperatures. Diphenylcarbene and Isobutene

Sir:

Reactions of triplet diphenylcarbene, Ph_2C , with olefins are readily observable at ambient temperature,^{1,2} whereas the analogous chemistry of phenylcarbene and phenylmethylcarbene becomes dominant only at very low temperatures.^{3,4} Notwithstanding the report that Ph_2C reacts with isobutene only by addition at 25 °C,^{1d} we find that both addition and "insertion" reactions compete effectively at 0 °C, albeit the former is dominant; cf. eq 1. We now report that (a) reaction



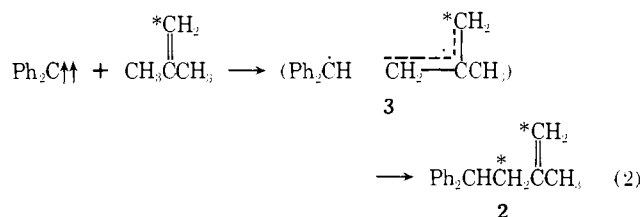
1 is dramatically temperature dependent, with **2** becoming the near-exclusive product at -196 °C; (b) alkene **2** is a true abstraction-recombination (a-r) product at -77 °C and probably also at -196 °C, although there the matrix imposes a "memory" effect on radical-pair recombination; and (c) the observed relation between $\ln(2/1)$ and T^{-1} implies that there is no enhancement of olefin formation³ when Ph_2C and isobutene react in the solid phase.

Photolysis at 0 °C of 0.116 M solutions of diphenyldiazomethane⁵ in isobutene gave 1,1-dimethyl-2,2-diphenylcyclopropane (**1**) and 2-methyl-4,4-diphenyl-1-butene (**2**) in a ratio of 3.2:1, eq 1.⁶ Also formed were benzophenone, benzophenone ketazine, and (<1%) diphenylmethane. Cyclopropane **1** was identified by NMR,^{1d} whereas authentic **2** was prepared by Yates' method,⁷ and was identical (GC, NMR,⁷ IR) with **2**⁸ isolated from reaction 1.

The temperature dependence of reaction 1 is illustrated by Table I; at -196 °C, olefin **2** was almost the sole $C_{17}H_{18}$ product detectable.⁹

To investigate the origin of **2**, diphenyldiazomethane was photolyzed in $^{13}CH_2=C(CH_3)_2$.¹⁰ In the ^{13}C NMR spectrum of **2**, C_1 and C_3 appear at δ_C^{TMS} 112.62 and 43.96, respectively. Intensity analyses of these signals, in standard and reaction product samples of **2**, afforded $^{13}C_3:^{13}C_1$ label distributions of 50:50 and 28:72, respectively, in **2** from -77 °C (solution) and -196 °C (matrix) photolyses.¹¹

The equidistribution of ^{13}C between C_1 and C_3 , observed in product **2** formed at -77 °C, establishes an a-r mechanism operating with complete equilibration of radical pair **3**; cf. eq 2. Label equilibration is significantly incomplete in the -196



°C matrix photolysis, with the direction of inequality suggesting a partial inhibition, by the matrix, of the relative motions needed within **3** to geometrically equilibrate C_3 and C_1 , relative to $Ph_2\overset{*}{C}H$. There is no evidence for triplet Ph_2C addition, followed by H migration, as an important origin of **2**.^{4,12} Such a mechanism would require an excess of ^{13}C at C_3 .

Figure 1 presents $\ln(2/1)$ as a function of T^{-1} . A least-squares correlation based on all five points ($r = 0.988$, significant at the 99% confidence level) yields $\Delta E_{app}^a(\text{arent}) = 1.1$