Some Reactions of *trans*-Hydridochlorobis(tricyclohexylphosphine)nickel(II), *trans*-$Ni(Cl)(H)[P(C_6H_{11})_3]_2$[1]

HOWARD C. CLARK AND ALAN SHAVER[2]
Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7

Received June 10, 1975

HOWARD C. CLARK and ALAN SHAVER. Can. J. Chem. **53**, 3462 (1975).

Some reactions of the title compound with several ligands, including olefins and acetylenes have been conducted and the new complexes *trans*-$[NiH\{P(C_6H_{11})_3\}_2L]BF_4$, L = methylpyridine or acetonitrile have been isolated. Although the bulky phosphine apparently hinders reaction sterically, with hexafluoro-2-butyne a product is obtained which is tentatively characterized as $Ni(CF_3C{\equiv}CCF_3)_3P(C_6H_{11})_3$. This compound is thought to contain the seven-membered ring nickelahexakis(trifluoromethane)cyclohepta-*cis,cis,cis*-triene. Pyrolysis of this compound yields hexakis(trifluoromethyl)benzene. A reaction of the nickel hydride also occurs with carbon monoxide in the presence of $TlBF_4$ to give $Ni(CO)_3P(C_6H_{11})_3$ and $[P(H)(C_6H_{11})_3]BF_4$. This reaction can be considered to result from the reductive elimination of $[P(H)(C_6H_{11})_3]Cl$.

HOWARD C. CLARK et ALAN SHAVER. Can. J. Chem. **53**, 3462 (1975).

On a effectué quelques réactions du composé mentionné dans le titre avec plusieurs ligands y compris des alcènes et des alcynes et on a isolé les nouveaux complexes $[NiH\{P(C_6H_{11})_3\}_2L]BF_4$-*trans*, où L = méthylpyridine ou acétonitrile. Quoique la volumineuse phosphine semble empêcher la réaction pour des raisons stériques, on a obtenu, avec l'hexafluorobutyne-2, un produit auquel on attribue provisoirement la structure $Ni(CF_3C{\equiv}CCF_3)_3P(C_6H_{11})_3$. On croit que ce composé contient le cycle à sept chaînons nickelahexakis(trifluorométhane)-cycloheptatriène-*cis,cis,cis*. La pyrolyse de ce composé fournit l'hexakis(trifluorométhyl) benzène. Une réaction de l'hydrure de nickel se produit aussi avec le monoxyde de carbone en présence de $TlBF_4$; il y a alors formation de $Ni(CO)_3P(C_6H_{11})_3$ et de $[P(H)(C_6H_{11})_3]BF_4$. On peut considérer que cette réaction provient d'une élimination réductive de $[P(H)(C_6H_{11})_3]Cl$.

[Traduit par le journal]

As part of a general interest in metal hydrides, we have been particularly concerned with the chemistry of neutral and cationic platinum hydrides (1, 2). The previously reported (3, 4) compound *trans*-$Ni(Cl)(H)(Cy_3P)_2$, where $Cy_3P = P(C_6H_{11})_3$, was chosen for study in an attempt to supply some comparisons to these platinum systems.

We hoped that the presence of the bulky phosphine ligands would help to stabilize reaction products, since σ-bonded hydride and carbon derivatives of nickel are often air sensitive and unstable at room temperature (3, 5).

Experimental

Inert atmosphere techniques were used. Solvents were generally dried over molecular sieves and purged with dry nitrogen before use; tetrahydrafuran and toluene were distilled from sodium–benzophenone under dry nitrogen just before use. *trans*-$Ni(Cl)(H)(Cy_3P)_2$ was prepared as previously reported (3).

Hydrido-4-methylpyridinebis(tricyclohexylphosphine)-nickel Tetrafluoroborate

trans-$Ni(Cl)(H)(Cy_3P)_2$, 0.378 g (0.50 mmol), was dissolved in 40 ml THF. 4-Methylpyridine, 0.6 ml (6.3 mmol) was added and a slight color change from yellow–brown to yellow occurred. $TlBF_4$, 0.146 g (0.50 mmol) was added in one portion and a white precipitate of TlCl formed immediately. The yellow reaction mixture was stirred at room temperature for 1 h, then filtered and stripped to a yellow oil which gave crystals upon pumping. These were extracted with 10 ml acetone and the solution filtered. Addition of ether and cooling to −78 °C caused the product to crystallize. It was collected on a fritte and washed with ether. Yield = 0.266 g (66.5%); decomposes at 165 °C *in vacuo*; i.r. ν(Ni—H) 1995 cm^{-1} (Nujol mull); n.m.r. (acetone) τ(Ni—H) 33.4 (triplet, J(P–H) = 139 Hz), τ(CH_2) 8.48 (multiplet), τ(CH_3) 7.50 (singlet), τ($NC_5H_4CH_3$) 2.48 and 1.16 (doublets, J = 6 Hz).

Anal. Calcd. for $C_{42}H_{72}NP_2NiBF_4$: C, 63.0; H, 9.25. Found: C, 63.2; H, 9.31.

Hydridoacetonitrilebis(tricyclohexylphosphine)nickel Tetrafluoroborate

This compound was prepared in an analogous manner. It was noted that if the $TlBF_4$ was added to the nickel

---

[1] Part XVI of the series, Chemistry of Metal Hydrides (for Part XV, see ref. 13).

[2] Present address: Department of Chemistry, McGill University, P.O. Box 6070, Station A, Montreal, Quebec.

complex in the absence of acetonitrile there was no reaction. However, addition of acetonitrile caused a rapid formation of TlCl. The product, isolated as above, decomposes above 150 °C; i.r. ν(Ni—H) 1992 cm^{-1} (Nujol mull); n.m.r. (acetone) τ(Ni—H) 31.6 (triplet, J(P-H) = 153 Hz), τ(CH_2) 8.42 (multiplet), τ(CH_3) 7.49 (singlet).

Anal. Calcd. for $C_{38}H_{70}NP_2NiBF_4$: C, 61.0; H, 9.37. Found: C, 61.0; H, 9.49.

Tricyclohexylphosphinetricarbonylnickel and Tricyclohexylphosphonium Tetrafluoroborate

trans-Ni(Cl)(H)($Cy_3P)_2$ (0.5 mmol) was dissolved in 20 ml THF. $TlBF_4$ (0.50 mmol) was added and carbon monoxide was bubbled into the yellow-brown slurry. There was an immediate precipitation of TlCl. The color changed first to lemon green, then after $\frac{1}{2}$ h treatment with CO, to pale blue. The reaction mixture was filtered and concentrated to about 2 ml. Addition of ether caused precipitation of a white product identified as P(H)-$(C_6H_{11})_3 \cdot BF_4$ (yield = 0.14 g, 76%). It was recrystallized from THF–ether, m.p. = 163 °C.

Anal. Calcd. for $C_{18}H_{34}PBF_4$: C, 58.7; H, 9.24. Found: C, 58.8; H, 9.26.

The THF–ether mother liquors from the reaction solution were stripped to dryness and recrystallized from a minimum of ether at −70 °C to give $Ni(CO)_3P(C_6H_{11})_3$, (yield > 60%, decomposes at 96 °C), which was identified by its infrared spectrum (6) and analysis.

Anal. Calcd. for $C_{21}H_{33}NiPO_3$: C, 59.6; H, 7.80. Found: C, 59.9; H, 8.00.

Reaction with Hexafluoro-2-butyne

trans-Ni(Cl)(H)($Cy_3P)_2$, 0.514 g (0.68 mmol) was dissolved in 20 ml toluene. The yellow-brown solution was frozen, the flask evacuated, isolated from the vacuum line, and allowed to warm at room temperature. Then $CF_3C\equiv CCF_3$ was admitted and the pressure adjusted to about 0.9 atm. The uptake of acetylene was monitored by means of a manometer and the pressure was readjusted to 0.9 atm by the admission of more acetylene as the reaction progressed. After stirring for about 1 h, an orange precipitate formed. After 3 h the reaction was complete and uptake of acetylene had ceased. The reaction mixture was filtered and the orange precipitate collected. The red mother liquors were concentrated to about 5 ml and cooled to −20 °C overnight to give 0.25 g of white crystals. These were readily sublimed at room temperature (10^{-2} Torr) (m.p. 206 °C (sealed capillary)) and were identified as hexakis(trifluoromethyl)benzene by means of the mass spectrum, infrared, and ^{19}F n.m.r. spectra (7) (yield = 76% based on Ni).

The orange precipitate was extracted with 10 ml CH_2Cl_2 and the solution filtered. Hexane (*ca.* 15 ml) was added and the solution cooled at −20 °C overnight and then to −40 °C for a further 4 h. Well-formed orange crystals were isolated by removing the mother liquors with a syringe and washing the crystals with cold hexane; yield = 0.28 g (50% assuming the formula $NiP(C_6H_{11})_3$-$(C_4F_6)_3$). The compound melts with decomposition at 128 °C. When a sample was heated to this temperature in an evacuated flask white crystals collected on a sublimation probe and were identified as hexakis(trifluoromethyl)benzene. Despite several attempts, reproducible analytical results for the complex could not be obtained. Analyses were conducted by Chemalytics, Tempe, Arizona; Spang Microanalytical Laboratory, Ann Arbor, Michigan; Midwest Microlab Indianapolis, Indiana, and Alfred Bernhardt, Elbach uber Engelskirchen, West Germany. The complex showed: i.r. (Nujol mull) 1675(w), 1645(m), 1616(w), 1330(s), 1300(s), 1262(vs), 1233(vs), 1195(vs), 1150(vs), 1100(s), 1005(w), 941(w), 730(m), 684(m), 663(m), 638(m); ^{19}F n.m.r. (CH_2Cl_2): peak A 50.1 p.p.m. (multiplet), peak B 54.9 p.p.m. (quartet, J = 8.8 Hz), peak C 59.6 p.p.m. (multiplet); A:B:C = 1:1:1. Double irradiation of C reduced A and B to singlets. Double irradiation of A reduced C to a quartet J = 8.8 Hz.

$NiP(C_6H_{11})_3(C_4F_6)_3$ analysis

		Found*			
	Calculated	*A*	*B*	*C*	*D*
C	43.7	42.6, 42.9	40.8, 41.7	40.2	40.0
H	4.00	3.74, 3.52	3.51, 3.48	3.77	3.8
F	41.5	—	48.1, 44.1	42.1	44.9
Molecular weight	824	—	841		

*The letters *A* to *D* represent different microanalytical laboratories.

Results and Discussion

The first reactions were attempts to remove the chloride ligand from *trans*-Ni(Cl)(H)($Cy_3P)_2$ and generate a solvated cationic metal hydride. In platinum systems this type of complex is quite reactive (1, 2, 8–10). Extensive decomposition occurred with $AgPF_6$ so $TlBF_4$ was used. However in contrast to the analogous platinum complex (9), the chloride could not be removed in THF or acetone solution. Instead the presence of a small, highly coordinating ligand was necessary to cause precipitation of TlCl and formation of complexes of the type *trans*-[Ni(H)(L)($Cy_3P)_2$]BF_4, where L = acetonitrile or 4-methylpyridine.

A color change from yellow-brown to yellow was observed when 4-methylpyridine was added to a solution of *trans*-$Ni(Cl)(H)(Cy_3P)_2$. Also there was no precipitation of TlCl from a slurry of $TlBF_4$ and *trans*-$Ni(Cl)(H)(Cy_3P)_2$ until one or two drops of acetonitrile were added. These two facts seem to imply coordination of the incoming ligand before the chloride is displaced. This is surprising since we felt that the large cone angle (11) of Cy_3P (180°) might inhibit the formation of a five-coordinate intermediate. This is apparently not the case, at least for small or narrow bases. Several other ligands were tested but all failed to displace the chloride under similar reaction conditions. These included trialkyl and aryl phosphines and some acetylenes. Attempts to displace the coordinated acetonitrile with some acetylenes were also unsuccessful.

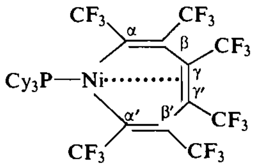
The reaction with carbon monoxide probably proceeds initially in the same way as the acetonitrile reaction. The first step is displacement of chloride and formation of *trans*-$[Ni(H)(CO)(Cy_3P)_2]BF_4$. In the presence of excess CO a reductive elimination occurs to give $Ni(CO)_3(Cy_3P)$ and $[PCy_3(H)]BF_4$.

Since a labile cationic nickel hydride complex could not be produced by abstraction of chloride from *trans*-$Ni(Cl)(H)(Cy_3P)_2$ a number of reactions of the complex itself with olefins and acetylenes were conducted. Again the complex proved somewhat unreactive; in most cases it was recovered unchanged. Although dimethylcarboxylate acetylene seemed to polymerize readily in the presence of the complex, no nickel–acetylene complex formation could be detected and starting material was recovered. However, hexafluoro-2-butyne reacts readily with the complex to give a mixture of products.

The mechanics of the reaction with C_4F_6 are important. In one experiment an excess of the acetylene was condensed onto the frozen toluene solution of the nickel complex and the mixture allowed to warm. As it became soft the acetylene layer was polymerized into a white perforated disk. The reaction was continued as usual and the normal products were obtained (see Experimental). The disk was removed from the flask with tweezers and found to be quite resistant to tearing. It was also insoluble in an assortment of common solvents. In another experiment the toluene was not allowed to warm sufficiently and C_4F_6 condensed in the liquid. The rapid stirring dispersed the liquid acetylene into fine droplets which polymerized to form tough white beads. After this polymerization, reaction continued normally.

In the usual reaction, the complex was dissolved in toluene at room temperature and exposed to 0.9 atm of C_4F_6. There was a smooth uptake of acetylene that gradually stopped over a period of 3 h. Much of this acetylene was converted to hexakis(trifluoromethyl)benzene (0.75 mol per mol of nickel). The gradual slowing of acetylene uptake was accompanied by the production of the orange nickel complex (50% yield).

Although we have experienced difficulty in obtaining reproducible analyses, the characterization of this complex has been aided by the report of a nickel complex (12) containing a nickelahexakis(trifluoromethyl)cyclohepta-*cis,trans,cis*-triene ring, whose stereochemistry was proven by X-ray analysis. The close similarity of the ^{19}F n.m.r. spectra of the two compounds leads us to propose a similar seven-membered ring for our complex. The exact stereochemistry must be decided by a crystal structure determination. However, since our orange complex yields hexakis(trifluoromethyl)benzene at 130 °C it seems reasonable to propose a *cis,cis,cis* structure as shown in **1**. A possible interaction (12) between nickel and the olefin across the ring is indicated with a dotted line. The quartet in the ^{19}F n.m.r. is assigned to the CF_3 in the α position while peaks C and A are assigned to the β and γ positions respectively.



1

The fact that hexakistrifluorobenzene (HTFB) and **1** are produced in 125% yield from starting nickel hydride is notable. **1** does not polymerize C_4F_6 when treated with the acetylene in freshly made THF or CH_2Cl_2 solutions. It is probable that a different nickel species acts as a cyclotrimerization catalyst and is also a precursor to **1**. As **1** is produced the concentration of the proposed catalyst decreases until all the nickel is converted to unreactive species. We have been unable to isolate compounds other than **1** and HFTB from the reaction mixture.

The demonstration that **1** is an intermediate in the production of HFTB is significant since similar structures are often proposed in the mechanism of cyclotrimerization of acetylenes by transition metals.

The financial support of the National Research Council of Canada and the award of an NRCC Postdoctorate Fellowship (to A.S. 1972–1974) are gratefully acknowledged.

1. H. C. CLARK and C. R. JABLONSKI. Inorg. Chem. **13**, 2213 (1974).
2. H. C. CLARK and C. S. WONG. J. Am. Chem. Soc. **96**, 7213 (1974).
3. M. L. H. GREEN, T. SAITO, and P. J. TANFIELD. J. Chem. Soc. A, 152 (1971).
4. K. JONAS and G. WILKE. Angew. Chem. Int. Ed. Engl. **8**, 519 (1969).
5. D. R. FAHEY. J. Organomet. Chem. Rev. A, **7**, 245 (1972).
6. C. A. TOLMAN. J. Am. Chem. Soc. **92**, 2953 (1970).
7. J. F. HARRIS, JR., R. J. HARDER, and G. N. SAUSEN. J. Org. Chem. **25**, 633 (1960).
8. H. C. CLARK and H. KUROSAWA. Inorg. Chem. **11**, 1275 (1972); **12**, 357 (1973); **12**, 1566 (1973).
9. T. G. ATTIG and H. C. CLARK. Can. J. Chem. This issue.
10. H. C. CLARK, C. R. JABLONSKI, and C. S. WONG. Inorg. Chem. **14**, 1332 (1975).
11. C. A. TOLMAN. J. Am. Chem. Soc. **92**, 2956 (1970).
12. J. BROWNING, M. GREEN, B. R. PENFOLD, J. L. SPENCER, and F. G. A. STONE. J. Chem. Soc. Chem. Commun. 31 (1973).
13. H. C. CLARK and H. KUROSAWA. Inorg. Chem. **12**, 1566 (1973).