charge-transfer interaction between the tribromide and disulfide moieties.

The structure provides some insight into the arrangement of Br_3^- in $(SNBr_{0.4})_x$. One of the terminal Br's would be expected to lie *in* the plane ($\bar{1}02$) of the $(SN)_x$ chain so as to maximize the type of interaction described in this paper. The orientation of the Br_3^- ion as a whole could then be either parallel or perpendicular to the chain. In either case, a nonbonded pair of the first Br would be directed at S. If the former (parallel) orientation were taken, this would allow both terminal Br atoms to interact with sulfur. Indeed, both electron diffraction[2] and spectroscopic[21] data suggest that whatever Br_3^- is present in $(SNBr_{0.4})_x$ (the question of the quantities of the various Br-containing species has not yet been resolved) is aligned parallel to *b*. This scheme not only provides a reason for that but would also predict that the Br_3^- is *in* the plane of the $(SN)_x$, not *between* the planes as would be required in a simpler intercalative model. In the absence of detailed knowledge of the MO picture of $(SN)_x$, this is, of course, speculative.

Registry No. $(S_4N_3^+)(Br_3^-)$, 67145-67-9.

Supplementary Material Available: A listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. L. Greene, G. B. Street, and L. J. Suter, *Phys. Rev. Lett.*, **34**, 577 (1975).
(2) G. B. Street, W. D. Gill, R. H. Geiss, R. L. Greene, and J. J. Mayerle, *J. Chem. Soc., Chem. Commun.*, 407 (1977).
(3) W. D. Gill, W. Bludau, R. H. Geiss, P. M. Grant, R. L. Greene, J. J. Mayerle, and G. B. Street, *Phys. Rev. Lett.*, **38**, 1305 (1978).
(4) J. Kuyper and G. B. Street, *J. Am. Chem. Soc.*, **99**, 7848 (1977).
(5) J. J. Mayerle, J. Kuyper, and G. B. Street, *Inorg. Chem.*, **17**, 2610 (1978).
(6) G. B. Street, R. L. Bingham, J. I. Crowley, and J. Kuyper, *J. Chem. Soc., Chem. Commun.*, 464 (1977).
(7) M. Akhtar, C. K. Chiang, A. J. Heeger, J. Milliken, and A. G. MacDiarmid, *Inorg. Chem.*, **17**, 1539 (1978).
(8) G. Wolmershäuser and G. B. Street, *Inorg. Chem.*, **17**, 2685 (1978).
(9) J. J. Mayerle, *Inorg. Chem.*, **16**, 916 (1977).
(10) The computer programs used were those mentioned in ref 9.
(11) "International Tables for X-Ray Crystallography", Vol. I, 3rd ed., Kynoch Press, Birmingham, England, 1969, p 99.
(12) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
(13) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2A.
(14) D. T. Cromer, "International Tables for X-Ray Crystallography", Vol. IV, Birmingham, England, 1974, Table 2.3.1.
(15) T. N. Guru Row and P. Coppens, *Inorg. Chem.*, **17**, 1670 (1978).
(16) C. Romers and E. W. M. Keulemans, *Proc. K. Ned. Akad. Wet., Ser. B*, **61**, 345 (1958), as quoted in ref 18.
(17) G. L. Breneman and R. D. Willett, *Acta Crystallogr.*, **23**, 467 (1967).
(18) G. L. Breneman and R. D. Willett, *Acta Crystallogr., Sect. B*, **25**, 1073 (1969).
(19) A. Hordvik, *Q. Rep. Sulfur Chem.*, **5**, 21 (1970).
(20) R. E. Rosenfield, Jr., R. Parthasarathy, and J. D. Dunitz, *J. Am. Chem. Soc.*, **99**, 4860 (1977).
(21) J. Macklin and G. B. Street, to be submitted for publication.

Contribution from the Department of Chemistry,
University of California, Los Angeles, California 90024

Simplified in Situ Syntheses of Anhydrous $HMn(CO)_5$

J. A. Gladysz,* Wilson Tam, G. M. Williams,
Dennis Lee Johnson, and David W. Parker

Received March 21, 1978

Hydride complexes of transition metals have played a critical role in the development of organometallic chemistry.[1,2] They are key intermediates in numerous stoichiometric and catalytic reactions and have been the object of a variety of structural,[3] spectroscopic, and theoretical studies.[1,2] A wide spectrum of methods has been utilized for their syntheses.[1,2]

One of the most extensively studied transition-metal hydrides has been $HMn(CO)_5$. Its physical properties have been examined in detail.[3-6] A number of novel and important manganese complexes have been synthesized from $HMn(CO)_5$,[7-12] and $HMn(CO)_5$ can be used to reduce organic compounds such as olefins and alkyl halides.[13]

In connection with several ongoing research projects, we required large amounts of anhydrous $HMn(CO)_5$ in THF. A literature survey revealed that most researchers employ the method of King.[14] This procedure is operationally cumbersome and requires (a) the generation of $Na[Mn(CO)_5]$ from $Mn_2(CO)_{10}$ and Na/Hg, (b) removal of mercury and solvent, (c) treatment of the $Na[Mn(CO)_5]$ residue with aqueous H_3PO_4, and (d) extensive vacuum line manipulations to separate H_2O and byproducts. A synthesis of $HMn(CO)_5$ from $Mn_2(CO)_{10}$ and H_2/CO (250 atm) at 200 °C has also been detailed.[15]

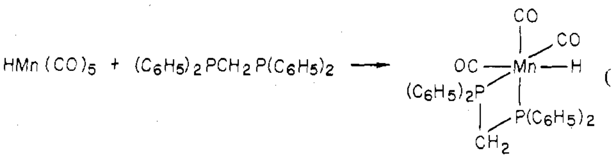
We report in this note the development of three rapid, convenient procedures for the in situ preparation of anhydrous $HMn(CO)_5$ in THF. They are complementary in terms of advantages and have been extensively used in our research group.

Results

Procedure A: $HMn(CO)_5$ from $Mn_2(CO)_{10}$. We recently described[16] a one-flask synthesis of $Li[Mn(CO)_5]$ from $Mn_2(CO)_{10}$ and $Li(C_2H_5)_3BH$[17] in THF. The formation of $Li[Mn(CO)_5]$ was found to be complete within a few minutes at room temperature. The only byproducts produced are H_2 and $(C_2H_5)_3B$, both of which are volatile. Consequently, it was of interest to determine if $HMn(CO)_5$ could be formed by protonation of $Li[Mn(CO)_5]$ in situ. For this purpose, an acid which was nonaqueous, nonoxidizing, and convenient to handle was sought. Trifluoromethanesulfonic acid (CF_3SO_3H)[18] was selected as meeting these criteria. Protonation of $Li[Mn(CO)_5]$ solutions, prepared as previously described,[16] with 1.1–1.2 equiv of CF_3SO_3H afforded $HMn(CO)_5$ in quantitative yield by IR (eq 1).

$$\begin{array}{l} Li(C_2H_5)_3BH + {}^1/_2Mn_2(CO)_{10} \rightarrow Li[Mn(CO)_5] + {}^1/_2H_2 + (C_2H_5)_3B \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow CF_3SO_3H \\ \qquad\qquad\qquad\qquad\qquad\qquad HMn(CO)_5 + Li^+CF_3SO_3^- \end{array} \quad (1)$$

The $HMn(CO)_5$ solutions prepared according to eq 1 were chemically characterized by reactions with $(C_6H_5)_2PCH_2P(C_6H_5)_2$, $Li(C_2H_5)_3BH$, and $(CO)_5Mn(COC_6H_5)$, as depicted in eq 2–4. Thus three types of characteristic $HMn(CO)_5$ reactions (substitution, deprotonation, and substrate reduction) could be achieved in high yield in situ.



1

(2)

$$HMn(CO)_5 + Li(C_2H_5)_3BH \rightarrow Li[Mn(CO)_5] + (C_2H_5)_3B + H_2 \quad (3)$$

$$HMn(CO)_5 + (CO)_5MnC({=}O)C_6H_5 \rightarrow HC({=}O)C_6H_5 + Mn_2(CO)_{10} \quad (4)$$

The synthesis of $HMn(CO)_5$ by procedure A yields $(C_2H_5)_3B$ and $Li^+CF_3SO_3^-$ as byproducts. For most preparative reactions utilizing $HMn(CO)_5$, these do not interfere. However, solvent and $HMn(CO)_5$ concentration may in some cases play important roles. For instance, acetylene hy-

0020-1669/79/1318-1163$01.00/0 © 1979 American Chemical Society

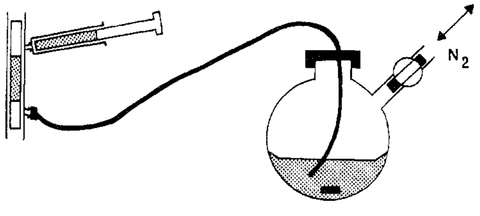


Figure 1. Apparatus for infrared monitoring of reactions.

drometalations effected with neat $HMn(CO)_5$[11] could not be repeated with $HMn(CO)_5$ solutions prepared by this procedure.

Procedure B: $HMn(CO)_5$ from Isolated $[Mn(CO)_5]^-$. This procedure was developed to enable the in situ preparation of $HMn(CO)_5$ free from $(C_2H_5)_3B$. One approach is to remove the solvent after $Li[Mn(CO)_5]$ formation as depicted in eq 1. The $(C_2H_5)_3B$ simultaneously volatilizes. The residue is then washed with a little hydrocarbon solvent and the $Li[Mn(CO)_5]$ redissolved in THF. Acidification with CF_3SO_3H is then executed as in eq 1.

An undoubtedly cleaner procedure, however, is to actually isolate $[Mn(CO)_5]^-$ as its crystalline PPN^+ (μ-nitrido-bis(triphenylphosphorus)) salt. We have recently published a preparation of $PPN[Mn(CO)_5]$[16b] and report here that it can be smoothly acidified by CF_3SO_3H as depicted in eq 5. Only the ionic byproduct $PPN^+CF_3SO_3^-$ is formed.

$$PPN[Mn(CO)_5] + CF_3SO_3H \rightarrow HMn(CO)_5 + PPN^+CF_3SO_3^- \quad (5)$$
$$PPN^+ = [(C_6H_5)_3P]_2N^+$$

We also reacted the $HMn(CO)_5$ prepared according to eq 5 with $(C_6H_5)_2PCH_2P(C_6H_5)_2$. Complete IR conversion to derivative **1** required 25 h, as opposed to the 5-min reaction observed previously (eq 2). Others have noted that $HMn(CO)_5$ undergoes substitution at variable rates and have obtained evidence for the operation of free radical chain mechanisms.[6]

Procedure C: $HMn(CO)_5$ from $(CH_3)_3Si[Mn(CO)_5]$. This procedure was developed to allow the in situ synthesis of $HMn(CO)_5$ free from ionic byproducts altogether. $(CH_3)_3Si[Mn(CO)_5]$ is a crystalline compound (mp 26.5 °C) which was first reported in 1969,[19] at which time its ability to undergo solvolysis in methanol was noted. We have recently published our method for the preparation of $(CH_3)_3Si[Mn(CO)_5]$[16b] and report here that it reacts quantitatively (^1H NMR) with 1 equiv of CH_3OH (no solvent) over the course of 8 h at 35 °C. $HMn(CO)_5$ and $(CH_3)_3SiOCH_3$ are produced according to eq 6. Thus $HMn(CO)_5$ may be

$$(CH_3)_3Si[Mn(CO)_5] + CH_3OH \rightarrow HMn(CO)_5 + (CH_3)_3SiOCH_3 \quad (6)$$

prepared with only an etheral, solventlike byproduct accompanying its formation.

Since $(CH_3)_3SiMn(CO)_5$ reacts with most oxygen-containing solvents, THF (if desired) must be added after the methanolysis step.

Apparatus. Although our procedures routinely afford high (>90%) yields of $HMn(CO)_5$ in the absence of spectroscopic monitoring, the simple apparatus detailed in Figure 1 allows reactions to be titrated to 100% yields. The reaction is conducted in a Schlenk flask which is fitted with a septum and a Teflon needle. A standard 0.1-mm cavity NaCl IR cell is mated to the other end of the needle with a machined Teflon plug. To the other IR cell inlet is attached a (gas-tight) syringe. A slight positive nitrogen pressure is maintained via the side arm of the Schlenk flask. By pumping of the syringe, the reaction mixture can be spectroscopically sampled at any time.

Thus by use of the apparatus depicted in Figure 1, the sequential addition of $Li(C_2H_5)_3BH$ and CF_3SO_3H to $Mn_2(CO)_{10}$ (eq 1) is readily monitored. Further reactions of $HMn(CO)_5$ (e.g., eq 2–4) are also conveniently followed. For instance, $Li(C_2H_5)_3BH$ rapidly converts $HMn(CO)_5$ back to $Li[Mn(CO)_5]$ (eq 3). By reprotonation with CF_3SO_3H, we were able to cycle between $Li[Mn(CO)_5]$ and $HMn(CO)_5$ several times without appreciable loss of material.

Comparison of Procedures. Only for procedure A is the organometallic starting material ($Mn_2(CO)_{10}$) commercially available. This method is the one of choice for preparative purposes. The synthesis of the starting material for procedure C ($(CH_3)_3Si[Mn(CO)_5]$) is rendered difficult by its sensitivity toward most oxygen-containing solvents. However, procedure C certainly affords the most innocuous byproduct and is the method of choice when the highest purity $HMn(CO)_5$ is sought.

The vacuum line isolation of $HMn(CO)_5$ described by King[14] should work equally well for $HMn(CO)_5$ prepared by procedures B and C. In our experience $(C_2H_5)_3B$ volatilizes with THF, and we have had no difficulty separating it from volatile organometallics such as $[(C_5H_5)Fe(CO)_2]CH_3$.[16b] Thus vacuum line purification of $HMn(CO)_5$ prepared by procedure A might also be possible. The whole point of this paper, however, is to describe methodology which makes such involved manipulations unnecessary.

Extensions. We have used a reaction sequence identical with that of procedure A to convert THF solutions of $[(C_5H_5)Mo(CO)_3]_2$ to $HMo(CO)_3(C_5H_5)$ in quantitative spectroscopic yield. However, the literature preparation of $HMo(CO)_3(C_5H_5)$[14a] is not particularly cumbersome. Unfortunately, similar attempts to synthesize $HFe(CO)_2(C_5H_5)$ were unsuccessful. We believe that CF_3SO_3H may prove to be a versatile reagent for the generation of transition-metal hydrides. To our knowledge, there is only one other report of its use to protonate a transition metal.[20]

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of dry N_2. Tetrahydrofuran was dried and deoxygenated by distillation from sodium benzophenone ketyl. $Li(C_2H_5)_3BH$ was purchased from Aldrich as a 1.0 M THF solution and used without further standardization. $PPN[Mn(CO)_5]$ and $(CH_3)_3Si[Mn(CO)_5]$ were prepared as previously described.[16b] $(C_2H_5)_2PCH_2P(C_6H_5)_2$ was purchased from PCR, Inc., and $(CO)_5Mn(COC_6H_5)$ was prepared by a modification[16] of the published procedure.[21] IR spectra were obtained on a Perkin-Elmer Model 521 spectrometer. ^1H NMR spectra were taken on a Varian T-60 spectrometer. Melting points were obtained on a Buchi Schmeltzpunkbestimmungsapparat and are uncorrected.

$HMn(CO)_5$ by Procedure A. In a typical reaction, $Mn_2(CO)_{10}$ (0.217 g, 0.557 mmol) was dissolved in 20 mL of THF in a Schlenk flask and the apparatus in Figure 1 assembled. $Li(C_2H_5)_3BH$ (1.3 mL, 1.3 mmol) was then added and the mixture stirred for 0.5 h. Injection of CF_3SO_3H (0.11 mL, 1.2 mmol) followed. IR sampling of the reaction mixture indicated quantitative formation of $HMn(CO)_5$ (2008 s, cm^{-1}).

***fac*-$HMn(CO)_3[(C_6H_5)_2PCH_2P(C_6H_5)_2]$.**[12a] $HMn(CO)_5$ (1.11 mmol) was prepared by procedure A. $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (0.425 g, 1.11 mmol) was dissolved in 10 mL of THF and added to the reaction mixture. After 5 min of stirring, the solvent was removed on a rotovap and the residue chromatographed on a silica gel column with 10% ethyl acetate in hexane (v/v). The product eluted rapidly (0.299 g, 0.646 mmol, 59% yield) and its IR spectrum (THF, 1995 (s), 1908 (vs) cm^{-1}) matched that previously reported.[12a] Benzene/hexane recrystallization afforded light yellow crystals; mp 145–147 °C.

Deprotonation of $HMn(CO)_5$. To 1.11 mmol of $HMn(CO)_5$, prepared by procedure A in the apparatus depicted in Figure 1, was added 1.2 mmol (1.2 mL) of $Li(C_2H_5)_3BH$. IR sampling of the reaction mixture indicated quantitative formation of $Li[Mn(CO)_5]$ (1898 (m), 1858 (s) cm^{-1}).

Reduction of $(CO)_5Mn(COC_6H_5)$. To 2 mmol of $HMn(CO)_5$ prepared by procedure A was added a solution of 2 mmol (0.600 g) of $(CO)_5Mn(COC_6H_5)$ in 10 mL of THF. After 10 min, the solvent was removed on a rotovap and the residue chromatographed on a silica gel column with 10% ethyl acetate in hexane (v/v). $Mn_2(CO)_{10}$ was obtained in 86% yield (0.671 g, 1.72 mmol). In a similar run, the reaction residue was treated with 2,4-dinitrophenylhydrazine according to a standard procedure.[23] Subsequently isolated was the 2,4-dinitrophenylhydrazone of benzaldehyde (mp 238–239 °C; 0.569 g, 99% yield).

$HMn(CO)_5$ by Procedure B. To 0.98 g (1.34 mmol) of PPN$[Mn(CO)_5]$ in 80 mL of THF was added 0.13 mL (1.51 mmol) of CF_3SO_3H. By use of the Schlenk apparatus in Figure 1, a spectroscopic yield of 100% was determined. After the addition of 0.512 g (1.34 mmol) of $(C_6H_5)_2PCH_2P(C_6H_5)_2$ to the above reaction mixture and 24 h of stirring, a 54% yield of *fac*-$HMn(CO)_3[(C_6H_5)_2PCH_2(C_6H_5)_2]$ was isolated by the procedure described previously.

$HMn(CO)_5$ by Procedure C. To a 5-mm NMR tube containing $(CH_3)_3Si[Mn(CO)_5]$ (0.127 g, 0.473 mmol) and *p*-di-*tert*-butylbenzene (0.0045 g, 0.024 mmol) was added dry methanol (0.0155 g, 0.484 mmol). The mixture was shaken until it was homogeneous and kept at 35 °C for 8 h. $HMn(CO)_5$ was formed in >97% yield by ^1H NMR. In normal preparative runs, the *p*-di-*tert*-butylbenzene standard was omitted. Solvents which have been added after the methanolysis is complete include THF, benzene, and acetone.

The sample of $HMn(CO)_5$ prepared above was cooled to −78 °C and allowed to warm to room temperature under vacuum. Benzene-d_6 (0.50 mL) was then added. The ^1H NMR spectrum showed that 87% of the $HMn(CO)_5$ and 24% of the $(CH_3)_3SiOCH_3$ remained. This experiment establishes that with proper vacuum line fractionation techniques, $HMn(CO)_5$ should be easily separable from $(CH_3)_3SiOCH_3$.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research through 1977. We thank the Department of Energy for subsequent funding.

Registry No. **1**, 36344-24-8; $HMn(CO)_5$, 16972-33-1; $Mn_2(CO)_{10}$, 10170-69-1; PPN$[Mn(CO)_5]$, 52542-59-3; $(CH_3)_3Si[Mn(CO)_5]$, 26500-16-3; $(CO)_5Mn(COC_6H_5)$, 15612-92-7; $Li[Mn(CO)_5]$, 15689-01-7; $Li(C_2H_5)_3BH$, 22560-16-3; CF_3SO_3H, 1493-13-6; CH_3OH, 67-56-1.

References and Notes

(1) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
(2) E. L. Muetterties, Ed., "Transition Metal Hydrides", Marcel Dekker, New York, 1971.
(3) E. A. McNeill and F. R. Scholer, *J. Am. Chem. Soc.*, **99**, 6243 (1977).
(4) P. S. Ireland, C. A. Deckert, and T. L. Brown, *J. Magn. Reson.*, **23**, 485 (1976).
(5) W. F. Edgell, J. W. Fischer, G. Asato, and W. M. Risen, *Inorg. Chem.*, **8**, 1103 (1969).
(6) B. H. Byers and T. L. Brown, *J. Organomet. Chem.*, **127**, 181 (1977); *J. Am. Chem. Soc.*, **99**, 2527 (1977).
(7) W. Beck and W. Danzen, *Z. Naturforsch., B*, **30**, 716 (1975), and references therein.
(8) W. A. Herrman, M. L. Ziegler, K. Weidenhammer, H. Biersack, K. K. Mayer, and R. D. Minard, *Angew. Chem., Int. Ed. Engl.*, **15**, 164 (1976).
(9) K. D. Bos, E. J. Bulten, J. G. Noltes, and A. L. Spek, *J. Organomet. Chem.*, **92**, 33 (1975).
(10) J. Grobe and R. Rau, *Z. Anorg. Allg. Chem.*, **414**, 19 (1975).
(11) B. L. Booth and R. G. Hargeaves, *J. Chem. Soc. A*, 2766 (1969).
(12) (a) F. W. Einstein, E. Enwall, N. Flitcroft, and J. M. Leach, *J. Inorg. Nucl. Chem.*, **34**, 885 (1972); (b) G. L. Booth and R. N. Haszeldine, *J. Chem. Soc. A*, 157 (1966).
(13) R. L. Sweany and J. Halpern, *J. Am. Chem. Soc.*, **99**, 8335 (1977).
(14) (a) R. B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York, 1965, p 158; (b) R. B. King and F. G. H. Stone, *Inorg. Synth.*, **7**, 198 (1963).
(15) W. Hieber and G. Wagner, *Z. Naturforsch., B*, **12**, 478 (1957); **13**, 339 (1958).
(16) (a) J. A. Gladysz, G. M. Williams, W. Tam, and D. L. Johnson, *J. Organomet. Chem.*, **140**, Cl (1977). (b) J. A. Gladysz, G. M. Williams, W. Tam, D. L. Johnson, D. W. Parker, and J. C. Selover, *Inorg. Chem.*, **18**, 553 (1979).
(17) Sold by the Aldrich Chemical Co. as a 1 M THF solution under the trade name Super Hydride.
(18) R. D. Howells and J. D. McCown, *Chem. Rev.*, **77**, 69 (1977).
(19) A. D. Berry and A. G. MacDiarmid, *Inorg. Nucl. Chem. Lett.*, **5**, 601 (1969). W. Malisch and M. Kuhn, *Chem. Ber.*, **107**, 979 (1974).
(20) T. C. Flood, E. Rosenberg, and A. Sarhangi, *J. Am. Chem. Soc.*, **99**, 4334 (1977).
(21) R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).
(22) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 5th ed., Wiley, New York, 1964, pp 253–254.

Contribution from the Istituto di Chimica Generale, University of Pisa, 56100 Pisa, Italy, and Istituto di Chimica Generale, University of Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, 43100 Parma, Italy

The Reaction of Nucleophiles with *cis*-$PtCl_2(CO)_2$. 1. Crystal and Molecular Structure of the Carbamoyl Complex Derived from the Reaction with Diisopropylamine

Daniela Belli Dell'Amico,[1] Fausto Calderazzo,*[1]
and Giancarlo Pelizzi[2]

Received July 20, 1978

It has been pointed out[3] that metal carbonyls having force constants higher than 17.2 mdyn/Å should react with amines to give carbamoyl derivatives. We have recently reported[4] that *cis*-$PtCl_2(CO)_2$ is characterized by two exceedingly high $\tilde{\nu}_{CO}$'s (2168 and 2127 cm^{-1} in toluene, with force constants of 19.01 and 18.3 mdyn/Å, respectively), thus making this compound a particularly appropriate candidate to further test this proposal. In addition, due to the limited number of known platinum(II) carbonyl derivatives, no carbamoyl complexes of platinum have been reported which were obtained by the direct reaction of amines on an uncharged carbonyl compound of this metal.[5]

We want now to report that *cis*-$PtCl_2(CO)_2$ reacts promptly with secondary amines in a ratio of 1:2 to give carbamoyl compounds. The molecular structure of the isopropyl derivative is presented in this paper.

Experimental Section

Infrared spectra were measured with a Perkin-Elmer Model 283 instrument. Solvents were carefully dried by conventional methods and distilled prior to use. Diisopropylamine was distilled over sodium. Dichlorodicarbonylplatinum(II) was prepared according to the previously described[4] procedure. All operations were carried out under an atmosphere of prepurified nitrogen.

Preparation of $[NH_2\text{-}i\text{-}Pr_2]^+[cis\text{-}PtCl_2(CON\text{-}i\text{-}Pr_2)CO]^-$ (1). The dicarbonyl derivative (1.17 g, 3.63 mmol) dissolved in 150 mL of toluene was treated with diisopropylamine (0.73 g, 7.21 mmol) dissolved in toluene (50 mL). After about 2 h, the resulting precipitate was filtered and dried in vacuo (1.04 g, 55% yield). Anal. Calcd for $C_{14}H_{30}Cl_2N_2O_2Pt$: C, 32.07; H, 5.77; Cl, 13.52. Found: C, 31.68; H, 6.09; Cl, 12.88. The colorless compound is sensitive to moisture and darkens in air. It is soluble in dichloromethane, slightly soluble in toluene, and very slightly soluble in heptane.

X-ray Analysis, Data Collection, and Refinement of Structure. The carbamoyl derivative (1) was recrystallized from a heptane–toluene mixture. Preliminary unit-cell dimensions and symmetry information were deduced from rotation and Weissenberg photographs. The crystals belong to the orthorhombic system, and their diffraction pattern exhibited the absences $h0l$, $l = 2n + 1$, $hk0$, $h = 2n + 1$, $0kl$, $k = 2n + 1$, which are consistent with the *Pbca* space group. Accurate unit-cell parameters, with estimated standard deviations, were determined by a least-squares refinement of the 2θ values for 15 reflections measured on an "on-line" single-crystal automated Siemens diffractometer. Crystal data are as follows: $a = 21.756$ (9) Å, $b = 14.707$ (6) Å, $c = 12.708$ (6) Å, $V = 4066.1$ Å^3, $Z = 8$, $D_{calcd} = 1.71$ g cm^{-3}; Mo Kα radiation, λ 0.71069 Å; μ(Mo Kα) = 75.2 cm^{-1}; $F(000) = 2048$.

Three-dimensional intensity data were taken at room temperature from a roughly prismatic crystal of approximate dimensions 0.15 ×

0020-1669/79/1318-1165$01.00/0