

The carbonylation chemistry of $[(\text{silox})_2\text{TaH}_2]_2$ (**1**) tracks the critical sequence of complicated reactions pertaining to the F-T mechanism (deoxygenation, H-C and C-C bond formation) and provides alternative views of certain heterogeneous transformations. Since **2** is formed directly, the generation of $(\text{CH}_2)_{\text{ads}}$ via H-transfer concomitant with or prior to C-O bond scission must still be considered;³⁰ the dissociative adsorption of CO may not be necessary. Most importantly, a C-O bond has been broken, reformed, and broken again in the conversion of **1** to **4**.³¹ Extrapolating to heterogeneous processes, oxygenated surfaces may serve as reservoirs for CH, CH_2 , and, presumably, CH_3 ³² functionalities via $(\text{OCH})_{\text{ads}}$,³³ $(\text{OCH}_2)_{\text{ads}}$,³⁴ and $(\text{OCH}_3)_{\text{ads}}$. Methylene units adsorbed on actual F-T surfaces are therefore *not constrained to be solely metal-bound*. Further mechanistic studies and characterizations of thermal, hydrogenation, and other carbonylation products are currently being undertaken.

Acknowledgment. Support from the Air Force Office of Scientific Research, Cornell University, Chevron Research Company, and the National Science Foundation (CHE-8308272) is gratefully acknowledged. We thank Mark M. Banaszak Holl for experimental assistance and the NSF and NIH for support of the Cornell NMR Facility.

(30) (a) Pichler, H.; Schultz, H. *Chem. Ing. Tech.* **1970**, *12*, 1160-1174. (b) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61-103.

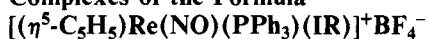
(31) A similar C-O bond breakage has been observed in the conversion of $\text{Cp}^*\text{TaH}(\eta^2\text{-CH}_2\text{O})$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) to $\text{Cp}^*\text{Ta}=\text{O}(\text{CH}_3)$, including evidence for a pre-equilibrium involving $\text{Cp}^*\text{Ta}(\text{OCH}_3)$. See: van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347-5349.

(32) In view of ref 31, the conversion of **3** to **4** may proceed via the following: (1) reductive elimination to form a $\mu\text{-OCH}_3$; (2) oxidative addition of the O-CH₃ bond, generating a Ta-CH₃; (3) Me transfer to $\mu\text{-CHO}$ concomitant with deoxygenation.

(33) Nijs, H. H.; Jacobs, P. A. *J. Catal.* **1980**, *66*, 401-411.

(34) Anton, A. B.; Parmeter, J. E.; Weinberg, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 1823-1833.

A General Class of Stable Alkyl Halide Complexes: Synthesis, Structure, and Reactivity of Alkyl Iodide Complexes of the Formula



Charles H. Winter, Atta M. Arif, and J. A. Gladysz*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received August 3, 1987

Of all of the common organic functional groups, alkyl halides (RX) have by far the least developed coordination chemistry.¹⁻³ To our knowledge isolable 1:1 adducts are unknown, although the *bis*(methyl iodide) complex $[(\text{H})_2\text{Ir}(\text{PPh}_3)_2(\text{ICH}_3)_2]^+\text{X}^-$ has been recently described by Crabtree.¹ The lack of stable alkyl halide complexes has generally been attributed to poor Lewis basicity

(1) (a) Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361. (b) Burk, M. J.; Segmuller, B.; Crabtree, R. H. *Ibid.* **1987**, *6*, 2241.

(2) For chelating aryl halide complexes $o\text{-C}_6\text{H}_4\text{X}(\text{DL}_n)$ ($\text{DL}_n = \text{PAR}_2$, S, Br, I), see ref 1 and the following: (a) Burk, M. J.; Crabtree, R. H.; Holt, E. M. *Organometallics* **1984**, *3*, 638. (b) Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2913. (c) Barceló, F.; Lahuerta, P.; Ubeda, M. A.; Foces-Foces, C.; Cano, F. H.; Martínez-Ripoll, M. *J. Chem. Soc., Chem. Commun.* **1985**, 43. (d) Solans, X.; Font-Altaba, M.; Aguiló, M.; Miravittles, C.; Besteiro, J. C.; Lahuerta, P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 841. (e) Cotton, F. A.; Lahuerta, P.; Sanau, M.; Schwotzer, W.; Solana, I. *Inorg. Chem.* **1986**, *25*, 3526. (f) Kulawiec, R. J.; Holt, E. M.; Lavin, M.; Crabtree, R. H. *Ibid.* **1987**, *26*, 2559. (g) Catala, R. M.; Cruz-Garriz, D.; Hills, A.; Hughes, D. L.; Richards, R. L.; Sosa, P.; Torrens, H. *J. Chem. Soc., Chem. Commun.* **1987**, 261.

(3) (a) A diene-chelated cyclopropyl bromide complex has recently been reported: Liotta, F. J., Jr.; Van Duyne, G.; Carpenter, B. K. *Organometallics* **1987**, *6*, 1010. (b) See, also: Cotton, F. A.; Ilsley, W. H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 3475.

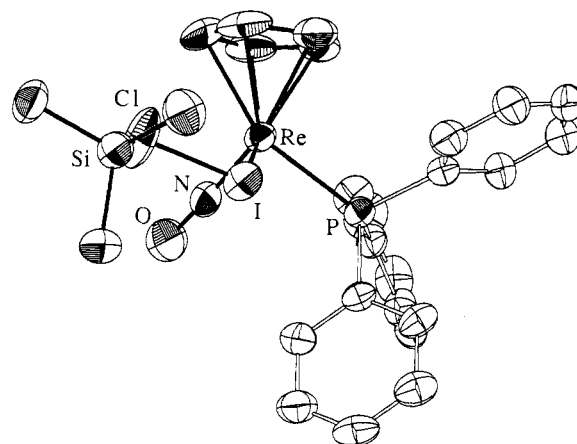


Figure 1. Structure of the cation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{ICH}_2\text{Si}(\text{CH}_3)_3)]^+\text{BF}_4^-\cdot(\text{CH}_2\text{Cl}_2)_{0.5}$ (**4d**· $(\text{CH}_2\text{Cl}_2)_{0.5}$). Selected bond lengths (Å) and angles (deg): Re-I, 2.678 (1); Re-P, 2.385 (3); Re-N, 1.740 (9); N-O, 1.20 (1); I-Cl, 2.18 (1); Cl-Si, 1.88 (2); I-Re-P, 91.82 (9); I-Re-N, 97.0 (4); P-Re-N, 91.1 (3); Re-N-O, 177 (1); Re-I-Cl, 102.5 (5); I-Cl-Si, 114.5 (9).

and/or the availability of facile decomposition pathways such as oxidative addition. In this communication, we report the synthesis and isolation of alkyl iodide complexes of the formula $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{IR})]^+\text{BF}_4^-$ and other data that suggest that alkyl halide complexes may be far more accessible than previously realized. Importantly, the coordination of alkyl halides to metals provides a new generation of leaving groups that can be easily modified and, as in the reported examples, rendered chiral.

We recently reported that the reaction of methyl complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3)$ (**1**) and $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (CH_2Cl_2 , -78°C) gave a reactive intermediate (stable to -20°C) formulated as the chiral pyramidal Lewis acid $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+\text{BF}_4^-$ (**2**) or the CH_2Cl_2 adduct $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{ClCH}_2\text{Cl})]^+\text{BF}_4^-$ (**3**).⁴ Subsequent ¹³C NMR experiments have provided good evidence for coordinated CH_2Cl_2 .^{4b} Hence, the reaction of **1** and $\text{HBF}_4\cdot\text{Et}_2\text{O}$ was followed by addition of alkyl iodides RI (3.0 equiv, Scheme I). New products formed upon warming (-40 to 0°C , ca. 95%, ³¹P NMR). Workup gave alkyl iodide complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{IR})]^+\text{BF}_4^-$ (**4**; R = CH_3 (a), CH_2CH_3 (b), $\text{CH}_2\text{CH}_2\text{CH}_3$ (c), $\text{CH}_2\text{Si}(\text{CH}_3)_3$ (d)) as analytically pure powders in 67-87% yields.⁵ The structures of **4a-d** followed from their spectroscopic properties and in particular from the downfield shifts exhibited by the ICH carbons and protons in ¹³C and ¹H NMR spectra.⁵ Oxidative addition products such as $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3)(\text{Br})]^+\text{X}^-$ show upfield ReCH^1H and ¹³C NMR resonances that are also strongly coupled to phosphorus.⁶

Crystals of the solvate **4d**· $(\text{CH}_2\text{Cl}_2)_{0.5}$ were grown from CH_2Cl_2 /hexanes, and the X-ray structure was determined (Figure 1) as described in the Supplementary Material. The carbon-iodine bond (2.18 (1) Å) is very slightly longer than that in ethyl iodide (2.139 (5) Å),⁷ and the Re-I bond (2.678 (1) Å) is shorter than

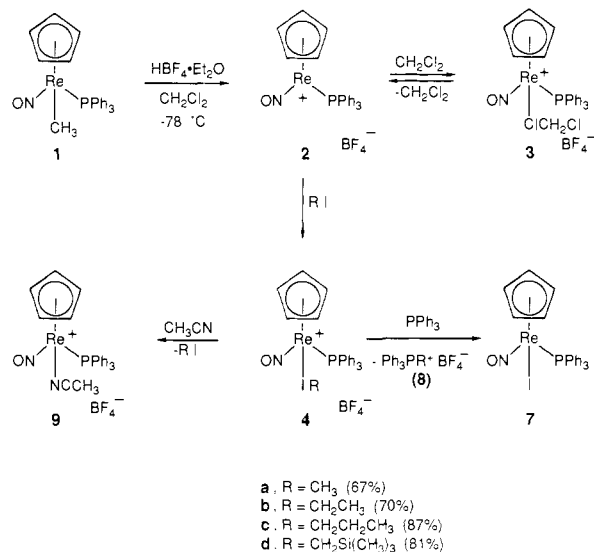
(4) (a) Fernández, J. M.; Gladysz, J. A. *Inorg. Chem.* **1986**, *25*, 2672. (b) Fernández, J. M., unpublished results.

(5) All new compounds were characterized by microanalysis, IR, and NMR (¹H, ¹³C, ³¹P) as described in the Supplementary Material. Selected NMR data (CD_2Cl_2) for **4b**, **10b** (-60°C), and **11b** (-40°C): ¹H NMR (δ) 5.62, 5.56, 5.59 (s, C_5H_5), 3.77, 4.18, 4.43 (dq, $J = 9, 7$ Hz, CHH'), 3.46, 3.73, 3.92 (dq, $J = 9, 7$ Hz, CHH'), 1.65, 1.62, 1.54 (t, $J = 7$ Hz, CH_3); ¹³C NMR (ppm) 92.1, 91.9, 91.5 (s, C_5H_5), 24.0, 56.7, 69.9 (d, $J = 3.1, \leq 2.0, 1.8$ Hz, CH_2), 18.8, 17.8, 17.5 (s, CH_3); ³¹P (ppm) 11.8, 12.9, 13.6 (s); NMR of ICH_2CH_3 (CD_2Cl_2) ¹H NMR (δ) 3.20 (q, $J = 7.5$ Hz, CH_2), 1.82 (t, $J = 7.5$ Hz, CH_3); ¹³C NMR (ppm) 20.89 (s, CH_3), -0.23 (s, CH_2).

(6) O'Connor, E. J., unpublished results, University of Utah; 192nd National Meeting of the American Chemical Society, Anaheim, CA, September 12, 1986; abstract INOR 347.

(7) Kasuya, T.; Oka, T. *J. Phys. Soc. Jpn.* **1960**, *15*, 296. For other $\text{CCH}_2\text{-I}$ bond lengths (2.13-2.14 Å), see: Williams, J. Q.; Gordy, W. *J. Chem. Phys.* **1950**, *18*, 994; Ghisalberti, E. L.; Jefferies, P. R.; Raston, C. L.; Skelton, B. W.; Stuart, A. D.; White, A. H. *J. Chem. Soc., Perkin Trans. 2* **1981**, 583.

Scheme I. Synthesis and Reactions of Alkyl Iodide Complexes



those in $(\text{CO})_4\text{Re}(\mu\text{-I})_2\text{Re}(\text{CO})_4$ and a related terminal iodide complex (2.81–2.83 Å).⁸ However, the structure is not appreciably distorted along an oxidative addition reaction coordinate, as the I–Re–P and I–Re–N bond angles (91.1–97.0°) are close to idealized octahedral values (90°). Bond angles in iodonium salts $\text{RR}'\text{I}^+\text{X}^-$ are typically ca. 95°, and a short I^+X^- “secondary bond” (2.5–3.5 Å) is usually found.⁹ In contrast, the Re–I–Cl bond angle in $4\text{d}\cdot(\text{CH}_2\text{Cl}_2)_{0.5}$ is 102.5 (5)°, and the BF_4^- fluorine atoms are ≥ 4.00 Å from the iodine. Finally, the P–Re–I–Cl torsion angle is 169°, which places the alkyl substituent in the region between the small NO and medium cyclopentadienyl ligands.

Thermal and chemical reactions of **4a–c** have been briefly studied. First, **4a–c** decompose over the course of 48 h in CD_2Cl_2 at 25 °C to give primarily the bridging halide complexes $(\text{SS}_2\text{-RR})\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\mu\text{-X})(\text{PPh}_3)(\text{NO})\text{Re}(\eta^5\text{-C}_5\text{H}_5)]^+\text{BF}_4^-$ (**5**, X = Cl,⁴ 28–43%; **6**, X = I, 46–61%; assayed by ¹H and ³¹P NMR with Ph_3SiCH_3 standard). The structure of new compound **6** was confirmed by an independent synthesis from iodide complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{I})$ (**7**)¹⁰ and Ag^+BF_4^- .¹¹ The mechanisms of formation of **5** and **6** are under investigation.

Reactions of **4a–c** with PPh_3 (1.2 equiv, 0.04 M in CDCl_3 , 25 °C, assayed as above) were complete within 15 min (Scheme I). Alkylation products $\text{Ph}_3\text{PR}^+\text{BF}_4^-$ (**8**, 93–86%) and iodide complex **7** (>99–95%) formed. Product identities were confirmed by ¹H and ³¹P NMR comparison to independently prepared authentic samples (Supplementary Material). Importantly, reactions of CH_3I , $\text{CH}_3\text{CH}_2\text{I}$, and $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ with PPh_3 under identical conditions were 70% complete after 4 h, and $\leq 10\%$ and $< 2\%$ complete after 18 h, respectively. Thus, coordinated alkyl iodides are markedly activated toward nucleophilic attack.

Reactions of **4a–c** with CH_3CN (2.0 equiv, 0.04 M in CD_2Cl_2 , 25 °C, assayed as above) were complete within 24 h (Scheme I). Displacement of the alkyl iodide ligand occurred to give **RI** (82–72%) and acetonitrile complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NCCCH}_3)]^+\text{BF}_4^-$ (**9**, 87–82%).¹² Small amounts of bridging

halide complexes **5** and **6** also formed. Product identities were confirmed by GLC and NMR comparison to authentic samples.

The synthesis of other alkyl halide complexes has been briefly explored. Analogous reactions of **1**, $\text{HBF}_4\cdot\text{Et}_2\text{O}$, and ethyl bromide or ethyl chloride gave ethyl halide complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{XCH}_2\text{CH}_3)]^+\text{BF}_4^-$ (**10b**, X = Br; **11b**, X = Cl). This structural assignment was made on the basis of ¹H, ¹³C, and ³¹P NMR spectra that closely match those of **4b**. Complexes **10b** and **11b** decompose between –20 and 0 °C. Analogous pentamethylcyclopentadienyl complexes also can be prepared and will be described in a later publication.

In summary, a variety of alkyl halide complexes are now readily accessible and can be expected to exhibit a rich and useful coordination chemistry.

Acknowledgment. We thank the NSF for support of this research and the NIH for a postdoctoral fellowship (C.H.W.).

Supplementary Material Available: Tables of data for new compounds⁵ and tables of crystallographic data, isotropic thermal parameters, bond lengths, bond angles, torsion angles, and anisotropic thermal parameters and a figure for $4\text{d}\cdot(\text{CH}_2\text{Cl}_2)_{0.5}$ (16 pages); table of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

Stereoselective Formation of Conjugated Enynes via Coupling of Alkynylidonium Tosylates and Vinylcopper Reagents

Peter J. Stang* and Tsugio Kitamura

Department of Chemistry, The University of Utah
 Salt Lake City, Utah 84112
 Received August 10, 1987

Conjugated enynes represent an important class of aliphatic compounds. They occur in a number of natural products¹ as well as provide an attractive route for stereospecific 1,3-diene synthesis.² Yet outside of Stille's³ recent, elegant report on the Pd-catalyzed direct coupling of acetylenic tin reagents with vinyl iodides and related Pd-mediated couplings,⁴ few methods are available for the simple formation of stereoisomeric 1,3-enynes.⁵

The current renaissance in tricoordinate iodine chemistry⁶ and the ready availability of new alkynylidonium salts,⁷ together with our recent success in the use of these species in the formation of hitherto unknown, unique, alkynyl esters,⁸ led us to explore their use in coupling reactions. Herein we report the stereoselective formation of 1,3-enynes, via a new carbon–carbon bond-forming reaction, involving the direct coupling of alkynylidonium tosylates **1** with alkenylcopper(I) reagents.

Alkynylphenyliodonium tosylates **1** are readily available in reasonable yields^{8a,9} by interaction of Koser's reagent,¹⁰ PhI-

(8) (a) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1979**, *170*, C15. (b) Darst, K. P.; Lenhart, P. G.; Lukehart, C. M.; Warfield, L. T. *Ibid.* **1980**, *195*, 317.

(9) (a) Khotsyanova, T. L. *Dokl. Akad. Nauk. SSSR* **1956**, *110*, 7. (b) Batchelor, R. J.; Birchall, R.; Sawyer, J. F. *Inorg. Chem.* **1986**, *25*, 1415. (c) Stang, P. J.; Surber, B. W.; Chen, Z.-C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228.

(10) Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

(11) (a) Fischer, E. O.; Moser, E. *Inorg. Synth.* **1970**, *12*, 35. (b) Symon, D. A.; Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1974**, 79.

(12) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.

(1) (a) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841. (b) Mori, K. *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1981.

(2) Zweifel, G.; Polston, N. L. *J. Am. Chem. Soc.* **1970**, *92*, 4068. Rossi, R.; Carpita, A.; Quirici, M. G.; Gandenzi, M. L. *Tetrahedron* **1982**, *38*, 361. Ulan, J. G.; Kuo, E.; Maier, W. F.; Rai, R. S.; Thomas, G. *J. Org. Chem.* **1987**, *52*, 3126. Ulan, J. G.; Maier, W. F.; Smith, D. A. *J. Org. Chem.* **1987**, *52*, 3132 and references therein.

(3) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138.

(4) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic: New York, 1985. Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.*, in press.

(5) Brown, H. C.; Molander, G. A. *J. Org. Chem.* **1981**, *46*, 646. Commercon, A.; Normant, J. F.; Villieras, J. *Tetrahedron* **1980**, *36*, 1215. Hoshi, M.; Masuda, Y.; Arase, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2855.

(6) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. Vargolis, A. *Synthesis* **1983**, 709. Vargolis, A. *Chem. Soc. Rev.* **1981**, *10*, 377. Banks, D. F. *Chem. Rev.* **1966**, *66*, 243.

(7) Koser, G. F. In *The Chemistry of Functional Groups, Supplement D*; Patai, S.; Rappoport, Z., Eds.; Wiley: 1983; Chapter 25, pp 1323–24.

(8) (a) Stang, P. J.; Surber, B. W.; Chen, Z. C.; Roberts, K. A. *J. Am. Chem. Soc.* **1987**, *109*, 228. (b) Stang, P. J.; Boehschar, M.; Lin, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 7832. (c) Stang, P. J.; Surber, B. W. *J. Am. Chem. Soc.* **1985**, *107*, 1452.