ELSEVIER

Journal of Organometallic Chemistry 485 (1995) 123–126

Journal of Organometallic Chemistry

Reaction of $(CO)_5W(THF)$ with triphenylmethyl azide and triptycyl azide

Scott T. Massey, Baubak Mansour, Lisa McElwee-White *

Department of Chemistry, Stanford University, Stanford, CA 94305, USA

Received 22 March 1994; in revised form 6 May 1994

Abstract

Reactions of $(CO)_5W(THF)$ with the sterically bulky azides RN_3 ($R = CPh_3$ or triptycyl) yield products that are consistent with decomposition of the transient zero-valence metal nitrene complexes $(CO)_5W{=}NR$. When $R{=}CPh_3$, triphenyl imine results from phenyl migration to the electrophilic nitrogen of the short-lived nitrene complex. When R=triptycyl, the migration pathway is shut down by ring constraints and triptycyl amine is formed, presumably via hydrogen abstraction by the highly reactive metal nitrene.

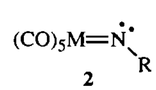
Keywords: Tungsten; Nitrenes; Azides

1. Introduction

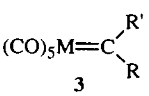
Metal imido complexes have recently been of great interest [1,2]. The more common complexes of high valence metals (**1**) generally contain a linear imido ligand with a strong metal–nitrogen triple bond. Although there are exceptions [3], reactivity in high-valence imido complexes generally occurs at sites other than the imido ligand. In contrast, zero-valence transition metal nitrene (imido) complexes of the form **2** are predicted by the EAN rule and EHT calculations [4] to have a metal–nitrogen double bond with a bent nitrene ligand and the resulting lone pair on nitrogen. Their electronic structures more closely resemble those of Fischer carbenes (**3**) than those of high valence imido complexes. This view of the bonding is consistent with experiments in which the transient species $(CO)_5W{=}NPh$ is trapped by nucleophiles and electrophiles [4]. Like the Fischer carbenes, $(CO)_5W{=}NPh$ undergoes reactions at the metal ligand multiple bond.

$L_nM'{\equiv}N{-}R$

1



2



3

(M' = high-oxidation state metal; L = ligand; M = Cr, W.)

Although there are extensive structural [5] and spectroscopic data [6] on high valence imido complexes, there have been no reports of isolated zero-valence metal nitrenes. However, complexes of the type $(CO)_nM{=}NR$ (M=Cr, Mo, W ($n = 5$) or Fe ($n = 4$)) have been invoked as reactive intermediates [7] and the related hydrazido complex $(CO)_5W{=}NNMe_2$ has been spectroscopically characterized [8]. Structural data for the hydrazido complex $(CO)_3(DPPE)W{=}NNMe_2$ are also available [9]. Nevertheless, in comparison with the well-documented chemistry of Fischer carbenes [10] and high valence metal imido complexes [1,2], little is known about the structure and chemical behavior of zero-valence metal nitrenes.

The reaction of organic azides with metal complexes is a well-precedented synthetic route to high valence imido complexes [1]. Coordination of an organic azide to a metal fragment activates the azide toward loss of N_2 to form a metal imido complex. There is also strong evidence that transient zero-valent metal nitrenes can be generated using this method [2b]. However, following reaction of organic azides with zero-valence complexes, the products decompose or undergo secondary reactions (both intramolecular and intermolecular) to yield new compounds. For example, the reaction between $Fe_2(CO)_9$ and MeN_3 results in tetraazadiene complex **4** as the major product [11], presumably from addition of a second equivalent of azide to a metal nitrene intermediate [12]. When PhN_3 is the reactant,

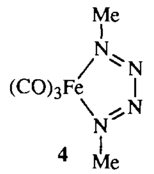
---

* Corresponding author at: Department of Chemistry, University of Florida, Gainesville, FL 32611, USA.

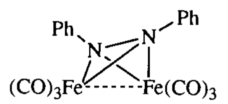
SSDI 0022-328X(94)24776-F

azobenzene complex **5** arises via dimerization of a metal nitrene. The ureylene complex **6** results when $(PPh_3)_3Pd(CO)$ is reacted with p-$CH_3C_6H_4SO_2N_3$ [13] and the reaction of $(CO)_3Ru(PPh_3)_2$ with $C_6H_5CON_3$ gives metal isocyanate **7** [14]. Although metal nitrenes were postulated as intermediates in these reactions, none were directly observed.

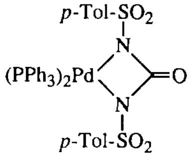
We now report the reaction between $(CO)_5W(THF)$ (THF = tetrahydrofuran) and bulky organic azides RN_3 (R=CPh_3 or triptycyl) to generate transient $(CO)_5W{=}NR$ species. Although related azide reactions that generate less sterically hindered transient nitrene complexes yield nitrene coupling products such as **4**–**7**, no coupling products were obtained from trityl or triptycyl azide. Instead, the electrophilic character of the nitrogen was exhibited in phenyl migration reactions in the trityl derivative. Upon suppression of the migration process in the triptycyl compound, triptycyl amine became the major organic product.



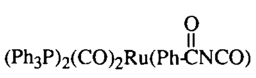
4



5



6



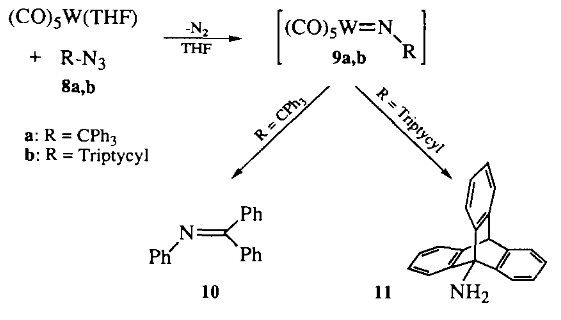
$(Ph_3P)_2(CO)_2Ru(Ph\text{-}\overset{\overset{O}{\|}}{C}NCO)$

7

2. Results and discussion

Trityl azide was found to react smoothly with $(CO)_5W(THF)$ over 5 days to give triphenyl imine as the major product with 32% yield (Scheme 1). No metal-containing products could be identified. Migration of a phenyl group in the free trityl nitrene to form an imine is a well-known rearrangement [15], but it has not previously been observed in a metal-coordinated system.

To render imine formation less favorable, triptycyl azide was employed as a reactant. The triptycyl group is similar to a trityl group but the phenyl rings are locked into a rigid polycyclic structure by a bridging methine unit. Although thermolysis or photolysis of triptycyl azide is postulated to form an unstable strained imine by loss of N_2 and ring expansion [16], this was not observed to be the case in the metal coordinated system. When triptycyl azide was reacted with $(CO)_5W(THF)$, triptycyl amine was found to be the major product with a 41% yield. Again, no organometallics could be identified. Control experiments showed that in the absence of $(CO)_5W(THF)$, the organic azides are indefinitely stable under the reaction conditions and also do not react with $W(CO)_6$.



Scheme 1.

As shown in Scheme 1, formation of triphenyl imine and triptycyl amine is consistent with the decomposition of zero-valent tungsten nitrene complexes. Bruce et al. [17] have reported similar results in the reaction between $Mo(CO)_3(CH_3CN)_2(PR_3)$ and 8-azidoquinoline in CH_3CN. When $PR_3 = PPh_3$, a phosphinimine complex is formed by migration of the phosphine ligand to an intermediate molybdenum(0) nitrene. However, when PR_3=$P(OMe)_3$ or $P(OEt)_3$, the migration pathway is suppressed. The primary product is then the amine complex $Mo(CO)_3(PR_3)[H_2N(C_9H_6N)]$, which is presumably formed through hydrogen abstraction by the intermediate metal nitrene. These results closely parallel the chemistry in our system. Migration of a phenyl group in the intermediate metal nitrene **9a** effectively traps the reactive nitrene species. The resulting imine complex is not stable under the reaction conditions and decomposes to give free triphenyl imine. The migration pathway is inhibited in **9b** because ring expansion in the triptycyl group would yield a strained bridgehead imine. In the absence of a facile migration pathway, **9b** scavenges hydrogen to give free triptycyl amine. The source of the amine hydrogen atoms is unknown. Similar results were obtained when Me_3P-$(CO)_4W(THF)$ and (DPPE)$(CO)_3W(THF)$ were reacted with trityl and triptycyl azide. Interestingly, no phosphine migration from the metal to the nitrene nitrogen to form phosphinimines was observed. Addition of a second equivalent of the azide to form a tetraazadiene complex [3a,12] also did not occur, presumably owing to steric hindrance from the trityl and triptycyl substituents.

Triphenylmethane (17% yield) and triptycene (5% yield) were also observed by ^1H NMR and gas chromatography (GC) mass spectrometry (MS) as minor products in their respective reaction mixtures. The formation of these products was a possible indication of metal attack at the terminal nitrogen of the organic azides (away from the sterically bulky R group) followed by N–R cleavage. C–N cleavage of organic azides has been observed in conjunction with formation of a stable metal azido [18] or nitrido [19] complex. However, $[(CO)_5WN_3]^-$ [20], the expected inorganic product of this process, could not be detected in the reaction mixtures. In fact, because of their incorporation into intractable material, the identity of the inorganic fragments could not be determined. Also, trace amounts of other organic products were detected by ^1H NMR and GC MS, but could not be identified.

Loss of N_2 and phenyl migration to form an imine is the major reaction pathway when trityl azide is photolyzed in the absence of metal compounds [15]. However, experiments designed to detect formation of free phenylnitrene from the transient complex $(CO)_5W{=}NPh$ uncovered no evidence for this process [21]. Generation of free nitrenes from the related complexes **9a** and **9b** is thus highly unlikely. There are nevertheless many well-known organic rearrangements (e.g. the Curtius rearrangement, the Schmidt reaction and the Beckmann rearrangement) involving migration of an alkyl or aryl group to electron-deficient nitrogen [22]. Since complexes of the type $(CO)_5W{=}NPh$ exhibit electrophilic behavior at nitrogen owing to their low-lying lowest unoccupied molecular orbitals with substantial coefficients at N [4], it is reasonable that the nitrene complexes would undergo similar rearrangements. Hydrogen abstraction by transient free nitrenes is also a known reaction [15]. To the extent that the electronic structure of the nitrene complexes resembles that of the electrophilic free nitrenes, the phenyl migration and amine formation pathways of free nitrenes would be accessible to the highly reactive **9a** and **9b**.

2.1. Summary

Triphenyl imine and triptycyl amine were the major products obtained in reactions between $(CO)_{5-n}L_nW$(THF) and trityl azide or triptycyl azide respectively. As these results are consistent with formation and decomposition of tungsten (0) nitrene species, it is reasonable to postulate that they arise from the nitrene complexes **9a** and **9b**. For the trityl compound, the mode of decomposition is phenyl migration to the electrophilic nitrene nitrogen. Ring constraints prevent aryl migration in the triptycyl derivative and hydrogen abstraction to form triptycyl amine becomes the major pathway.

3. Experimental section

Sample preparation and manipulation were performed in an inert atmosphere dry box. THF was distilled over sodium–benzophenone. THF-d_8 was vacuum transferred from sodium–benzophenone and stored over 3 Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-400 NMR spectrometer and IR spectra were recorded on an IBM IR/90 Fourier transform IR spectrometer. Analytical GC was performed on a Hewlett–Packard 5890A chromatograph equipped with a 5 m × 0.25 mm SE-30 capillary column and GC–MS was performed on a Hewlett–Packard 5970 GC MS instrument containing a 25 m × 0.20 mm SE-30 capillary column. $W(CO)_6$, $(CO)_4W$(DPPE), triphenylmethane and triptycene were purchased from Aldrich and used without further purification.

3.1. Generation of $(CO)_{5-n}L_nW(THF)$ complexes

$W(CO)_6$ (or the appropriate metal phosphine $W(CO)_{6-n}L_n$) was dissolved in freshly distilled THF in a Schlenk tube or an NMR tube equipped with a vacuum adapter. The solution was degassed by three freeze–pump–thaw cycles and irradiated with a Hanovia medium pressure mercury vapor lamp in a Pyrex immersion well. The samples were periodically degassed by further freeze–pump–thaw cycles to remove CO. The reaction progress could be monitored by IR by observing the disappearance of the $W(CO)_6$ signal at 1976 cm^{-1}. When phosphine derivatives were used, the reaction was monitored by ^1H NMR. Photolysis was stopped when half the starting material had been converted to the THF complex.

*3.2. Trityl azide (**8a**)*

Trityl azide was prepared by a literature method [23]. ^1H NMR (THF-d_8): δ 7.30 (m).

*3.3. Triphenyl imine (**10**)*

Triphenyl imine was prepared by the condensation of benzophenone with aniline in the presence of 3 Å molecular sieves. ^1H NMR (CD_2Cl_2): δ 7.75 (d, 2H), 7.49 (t, 1H), 7.41 (t, 2H), 7.28 (m, 3H), 7.11 (m, 4H), 6.91 (t, 1H), 6.70 (d, 2H).

*3.4. Triptycyl azide (**8b**)*

Triptycyl azide was prepared by a literature method [16]. ^1H NMR (THF-d_8): δ 7.56 (d, 3H), 7.41 (d, 3H), 7.05 (m, 6 H), 5.51 (s, 1H).

3.5. Triptycyl amine (11)

Triptycyl amine was prepared by the reduction of triptycyl azide with $LiAlH_4$ by a literature method [24]. ^1H NMR (THF-d_8): δ 7.50 (d, 3H), 7.40 (d, 3H), 7.06 (m, 6H), 5.39 (s, 1H), 3.07 (broad s, 2H).

3.6. $(CO)_5W(PMe_3)$

$(CO)_5W(PMe_3)$ was prepared by a literature method [25]. ^1H NMR (THF-d_8): δ 1.70 (d).

3.7. GC analysis of reaction products

$(CO)_5W(THF)$ was generated from 1.5 g of $W(CO)_6$ in 90 ml of THF according to the method described above. The solution was reduced to 40 ml under vacuum and then brought into a dry box. Aliquots (5 ml each) of the $(CO)_5W(THF)$ solution were added to vials containing 52.1 mg of trityl azide and 49.5 mg of triptycyl azide respectively. After 1 week, the reaction mixtures were exposed to air for 24 h and filtered. An internal standard solution (1 ml of 0.07813 M naphthalene in THF) was added to each of the reaction mixtures. THF was then added to bring the volume of the reaction mixtures to 5 ml. GC analysis of multiple reactions (six duplicate determinations per sample) gave yields varying by no more than 5%.

Acknowledgements

Funding for this work was provided by the U.S. Army Research Office, the Office of Naval Research, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation–Materials Research Laboratory Program through the Center for Materials Research at Stanford University.

References

[1] W.A. Nugent and J.M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley–Interscience, New York, 1988.

[2] (a) W.A. Nugent and B.L. Haymore, *Coord. Chem. Rev., 31* (1980) 123; (b) S. Cenini and G. La Monica, *Inorg. Chim. Acta., 18* (1976) 279; (c) A.J. Nielson, *Chem. N.Z.*, (1988) 131.

[3] (a) R.I. Michelman, R.G. Bergman and R.A. Andersen, *Organometallics, 12* (1993) 2741; (b) P.J. Walsh, A.M. Baranger and R.G. Bergman, *J. Am. Chem. Soc., 114* (1992) 1708; (c) D.S. Glueck, J. Wu, F.J. Hollander and R.G. Bergman, *J. Am. Chem. Soc., 113* (1991) 2041; (d) D.A. Evans, M.M. Faul and M.T. Bilodeau, *J. Org. Chem., 56* (1991) 6744; (e) A.O. Chong, K. Oshima and K.B. Sharpless, *J. Am. Chem. Soc., 99* (1977) 3420.

[4] B.A. Arndtsen, H.F. Sleiman, A.K. Chang and L. McElwee-White, *J. Am. Chem. Soc., 113* (1991) 4871.

[5] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, (1989) S1.

[6] (a) D.C. Bradley, S.R. Hodge, J.D. Runnacles, M. Hughes, J. Mason and R.L. Richards, *J. Chem. Soc., Dalton Trans.*, (1992) 1663; (b) J.A. Osborn and J.P.L. Ny, *Organometallics, 10* (1991) 1546; (c) W.P. Griffith, A.J. Nielson and M.J. Taylor, *J. Chem. Soc., Dalton Trans.*, (1988) 647.

[7] (a) R.S. Pilato, G.D. Williams, G.L. Geoffroy and A.L. Rheingold, *Inorg. Chem., 27* (1988) 3665; (b) L.S. Hegedus and A. Kramer, *Organometallics, 3* (1984) 1263; (c) L.S. Hegedus and B.R. Lundmark, *J. Am. Chem. Soc., 111* (1989) 9194; (d) J.W. Herndon and L.A. McMullen, *J. Organomet. Chem., 368* (1989) 83; (e) H. Alper, J.E. Prickett and S. Wollowitz, *J. Am. Chem. Soc., 99* (1977) 4330; (f) H. Alper and J.E. Prickett *J. Chem. Soc., Chem. Commun.*, (1976) 191.

[8] H.F. Sleiman, B.A. Arndtsen and L. McElwee-White, *Organometallics, 10* (1991) 541.

[9] B.A. Arndtsen, T.K. Schoch and L. McElwee-White, *J. Am. Chem. Soc., 114* (1992), 7041.

[10] K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert and K. Weiss, *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim 1983.

[11] M. Dekker and G.R. Knox, *Chem. Commun.*, (1967) 1243; (b) R.J. Doedens, *Chem. Commun.*, (1968) 1271.

[12] W.C. Trogler, *Acc. Chem. Res., 23* (1990) 426.

[13] W. Beck, W. Rieber, S. Cenini, F. Porta and G. La Monica, *J. Chem. Soc., Dalton Trans.*, (1974) 298.

[14] S. Cenini, M. Pizzotti, F. Porta and G. La Monica, *J. Organomet. Chem., 88* (1975) 237.

[15] F.D. Lewis and W.H. Saunders, Jr., in W. Lwowski (ed.), *Nitrenes*, Wiley–Interscience, New York, 1970, p. 47.

[16] H. Quast, P. Eckert and B. Seiferling, *Just. Liebigs' Ann. Chem.*, (1985) 696, and references cited therein.

[17] A.E. Bruce, M.R.M. Bruce, A. Saravanamuthu, J.L. Fourquet and M. Leblanc, *Inorg. Chem., 30* (1991) 3241.

[18] (a) R.K. Rosen, *Ph.D. Thesis*, University of California, Berkeley, CA, 1989; (b) P.C. Bevan, J. Chatt, J.R. Dilworth, R.A. Henderson and G.J. Leigh, *J. Chem. Soc., Dalton Trans.*, (1982) 821; (c) J. Chatt and J.R. Dilworth, *J. Chem. Soc., Chem. Commun.*, (1975) 983; (d) J.H. Osborne, A.L. Rheingold and W.C. Trogler, *J. Am. Chem. Soc., 107* (1985) 7945.

[19] (a) J. Fawcett, R.D. Peacock, and D.R. Russell, *J. Chem. Soc., Dalton Trans.*, (1987) 567; (b) C.J. Barner, T.J. Collins, B.E. Mapes and B.D. Santarsiero, *Inorg. Chem., 25* (1986) 4322; (c) J. Chatt and J.R. Dilworth, *J. Chem. Soc., Chem. Commun.*, (1974) 517.

[20] R.M. Dahlgren and J.I. Zink, *Inorg. Chem., 18* (1979) 597.

[21] H.F. Sleiman, S. Mercer and L. McElwee-White, *J. Am. Chem. Soc., 111* (1989) 8007.

[22] (a) J. March, *Advanced Organic Chemistry*, Wiley–Interscience, New York, 3rd edn., 1985, p. 982; (b) T.S. Stevens and W.E. Watts, *Selected Molecular Rearrangements*, Van Nostrand Reinhold, New York, 1973, p. 43.

[23] W.H. Saunders, Jr. and J.C. Ware, *J. Am. Chem. Soc., 80* (1958) 3328.

[24] J.H. Boyer, *J. Am. Chem. Soc., 73* (1951) 5865.

[25] R. Mathieu, M. Lenzi, and R. Poilblanc, *Inorg. Chem., 9* (1970) 2030.