

Preliminary communication

INSERTION REACTIONS OF A TUNGSTEN HYDRIDE COMPLEX

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Summary

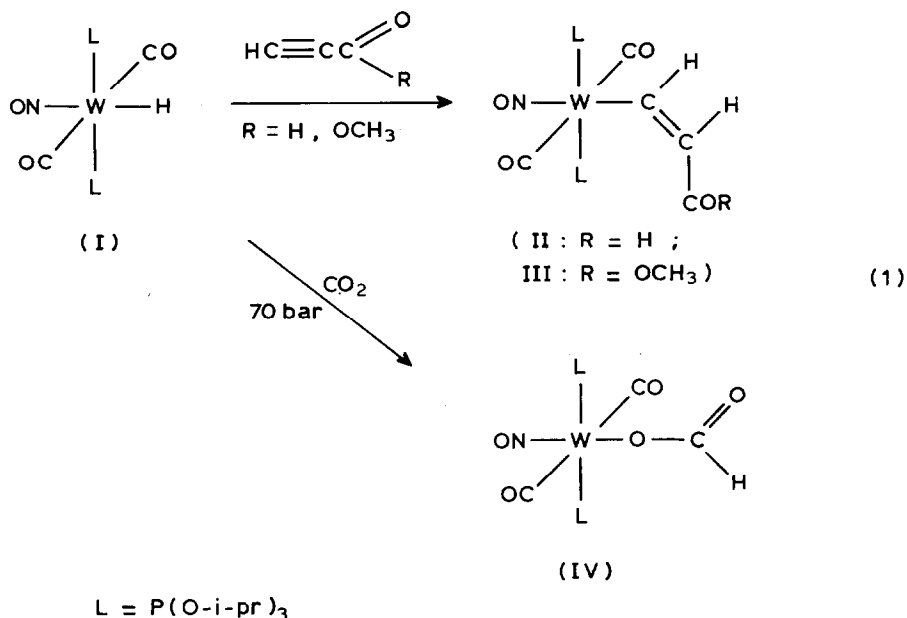
The W-H bond of a dicarbonylhydridonitrosylbis(triisopropylphosphite)tungsten complex is sufficiently weak to allow insertion of electron-poor acetylenes such as propiolic aldehyde and methylpropiolate, to give vinyltungsten compounds or insertion of CO₂ to give a formate species.

In general octahedral transition metal hydride complexes exhibit only a low propensity towards insertion of small molecules because of the strength of the M-H bond [1]. However, it was stated by Bursten et al. [2] that pseudo-octahedral nitrosyl substituted hydride compounds contain weak M-H bonds, and we recently synthesized a new class of nitrosyl substituted tungsten hydride complexes which from the IR frequency of the W-H vibration, we judged to contain a weak W-H bond which might give rise to enhanced reactivity [3]. In order to confirm this the dicarbonylbis(triisopropylphosphite)nitrosyltungsten hydride, (I), was treated at room temperature with the activated acetylene compounds propiolic aldehyde and methylpropiolate, and found to give *cis*-vinyltungsten derivatives (II and III) [4] (see eq. 1).

The assignment of the structures of II and III is based on IR and NMR data. The (OC)₂(ON)[P(O-*i*-pr)₃]₂W fragments in II and III give IR spectra in the $\nu(\text{C}\equiv\text{O})$ and $\nu(\text{N}\equiv\text{O})$ regions and NMR spectra for the phosphite ligands which are similar to those of I [5].

The olefinic hydrogens in II and III are in a *cis* disposition as shown by the low $J(\text{H}-\text{H})$ coupling constants. This indicates that *trans*-addition of the W-H bond across the acetylenic double bond has occurred, in much the same way as in the hydrostannation of alkynes [6]. This resemblance to hydrostannation suggests to us that these insertions into W-H bonds probably follow a radical pathway.

The high reactivity of the W-H bond in I is confirmed by the reaction with CO₂ [7,8]; treatment of I with liquid CO₂ (70 bar) at room temperature gave the η^1 -formate complex IV [9]. As for II and III, the composition and configuration of the W(CO)₂(NO)[P(O-*i*-pr)₃]₂ fragment in IV can be unambiguously deduced from



the IR, NMR and mass spectroscopic data, and the presence of a formate ligand is confirmed by characteristic ^1H and ^{13}C NMR resonances [10]. I also reacts with a variety of organic carbonyl compounds, and further studies are currently underway in our laboratory.

Acknowledgements

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References

- 1 H.D. Kaesz and B. Saillant, *Chem. Rev.*, 72 (1972) 231.
- 2 B.E. Bursten and M.G. Gatter, *J. Am. Chem. Soc.*, 106 (1984) 2554.
- 3 H. Berke and P. Kundel, *Z. Naturforsch. B*, 41 (1986) 527.
- 4 II and III were prepared by treating pentane solutions of I at room temperature with a slight excess of the appropriate acetylene derivative. Yellow crystals were obtained upon cooling the solutions to -70°C .
- 5 Selected analytical data:
 II: IR $\nu(\text{C}=\text{O})$, $\nu(\text{N}=\text{O})$ (n-pentane): 1958s, 1627m cm^{-1} . ^1H NMR (CD_3COCD_3): δ 9.62 ppm (t, $J(\text{P}-\text{H})$ 1.1 Hz, CHO), 6.88 ppm (t, d, $J(\text{P}-\text{H})$ 3.4 Hz, $J(\text{H}-\text{H})$ 1.3 Hz, $\text{W}-\text{CH}=\text{CH}$), 6.85 ppm (t, d, $J(\text{P}-\text{H})$ 2.4 Hz, $J(\text{H}-\text{H})$ 1.3 Hz, $\text{W}-\text{CH}=\text{CH}$), 4.68-4.55 ppm (m, P-O-CH), 1.29 ppm (d, $J(\text{H}-\text{H})$ 6.1 Hz, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 211.1 ppm (t, $J(\text{P}-\text{C})$ 10.3 Hz, CO), 204.31 ppm (s, CHO), 178.81 ppm (t, $J(\text{P}-\text{C})$ 16.2 Hz, $\text{W}-\text{C}=\text{C}$), 151.07 ppm (t, $J(\text{P}-\text{C})$ 5.8 Hz, $\text{W}-\text{C}=\text{C}$), 69.65 ppm (s, P-O-C), 24.22 ppm (s, CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): 127.64 ppm (s). MS: $m/e = 741$ [M] $^+$, $m/e = 713$ [$M-\text{CO}$] $^+$, $m/e = 685$ [$M-2\text{CO}$] $^+$, $m/e = 655$ [$M-2\text{CO}-\text{CH}_2\text{O}$] $^+$, $m/e = 630$ [$M-2\text{CO}-\text{C}_3\text{H}_3\text{O}$] $^+$.

III: IR $\nu(\text{C}\equiv\text{O})$, $\nu(\text{N}\equiv\text{O})$ (n-pentane): 1960s, 1700w, 1626m cm^{-1} . ^1H NMR (C_6D_6): δ 7.09 ppm (t, d, $J(\text{P}-\text{H})$ 3.23 Hz, $J(\text{H}-\text{H})$ 5 Hz, $\text{W}-\text{CH}=\text{CH}$), 6.27 ppm (t, d, $J(\text{P}-\text{H})$ 2.9 Hz, $J(\text{H}-\text{H})$ 5 Hz, $\text{W}-\text{CH}=\text{CH}$), 4.98–4.61 ppm (m, $\text{P}-\text{OCH}$), 3.58 ppm (s, COOCH_3), 1.28 ppm (d, $J(\text{H}-\text{H})$ 6.1 Hz, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 210.61 ppm (t, $J(\text{P}-\text{C})$ 10.3 Hz, CO), 177.72 ppm (s, COOR), 167.12 ppm (t, $J(\text{P}-\text{C})$ 15.5 Hz, $\text{W}-\text{C}=\text{C}$), 138.71 ppm (t, $J(\text{P}-\text{C})$ 5.9 Hz, $\text{W}-\text{C}=\text{C}$), 69.59 ppm (s, $\text{P}-\text{O}-\text{C}$), 50.44 ppm (s, OCH_3), 24.11 ppm (s, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 129.08 ppm (s). MS: $m/e = 771 [M]^+$, 743 $[M - \text{CO}]^+$, 715 $[M - 2\text{CO}]^+$, 684 $[M - 2\text{CO}, -\text{OCH}_3]^+$, 630 $[M - 2\text{CO}, -\text{C}_4\text{O}_2\text{H}_5]^+$.

Satisfactory elemental analyses were obtained.

- 6 A.J. Leusink and H.A. Budding, *J. Organomet. Chem.*, 11 (1968) 533; H.G. Kuivila, *Synthesis*, (1970) 499.
- 7 D.J. Darensbourg and R.A. Kudarowski, *Adv. Organomet. Chem.*, 22 (1983) 129; I.S. Kolomnikov and M.Kh. Grigoryan, *Russ. Chem. Rev.*, 47 (1978) 334; S. Gambarotta, S. Strologo, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc.*, 107 (1985) 6278.
- 8 See also the reaction of $\text{W}(\text{CO})_2(\text{NO})[\text{PPh}_3]_2\text{H}$ with C_3O_2 , G.L. Hillhouse, *J. Am. Chem. Soc.*, 107 (1985) 7772.
- 9 I was sealed with dry ice in a laboratory autoclave. After two days at room temperature (70 bar CO_2 pressure) the pressure was released and IV was obtained as yellow crystals by recrystallization from pentane.

10 Selected analytical data:

IV: IR $\nu(\text{C}\equiv\text{O})$, $\nu(\text{N}\equiv\text{O})$ (n-pentane): 2052w, 1961s, 1629s cm^{-1} . ^1H NMR (C_6D_6): δ 8.30 ppm (t, $J(\text{P}-\text{H})$ 1.5 Hz, OCOH), 4.5–4.6 ppm (m, $\text{P}-\text{O}-\text{CH}$), 1.25 ppm (d, $J(\text{H}-\text{H})$ 6.1 Hz, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 209.16 ppm (t, $J(\text{P}-\text{C})$ 10.3 Hz, CO), 166.43 ppm (s, OCO), 69.98 ppm (s, $\text{P}-\text{O}-\text{C}$), 24.19 ppm (s, CH_3). MS: $m/e = 703 [M - \text{CO}]^+$, 675 $[M - 2\text{CO}]^+$, 644 $[M - \text{CO}, -\text{OC}_3\text{H}_7]^+$, 616 $[M - 2\text{CO}, -\text{OC}_3\text{H}_7]^+$, 573 $[M - 2\text{CO}, -\text{OC}_3\text{H}_7, -\text{C}_3\text{H}_7]^+$, 485 $[M - 2\text{CO}, -\text{OC}_3\text{H}_7, -2\text{C}_3\text{H}_7, -\text{CO}_2\text{H}]^+$.

Satisfactory elemental analyses were obtained.