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SYNTHESIS OF TUNGSTEN ALKOXY-HYDRAZIDO(2-) COMPLEXES WITH TRANSITION METAL CARBONYL COMPLEX ANION

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The dinitrogen complex trans-$[W(N_2)_2(dpe)_2]$ (dpe = 1,2-bis(diphenylphosphino)ethane) reacted with $HCo(CO)_4$ or $HFeCo_3(CO)_{12}$ in the presence of alcohols to give alkoxy-hydrazido(2-) complexes, $[W(OR)(NNH_2)(dpe)_2]^+[A]^-$ (A = $Co(CO)_4$, R = CH_3, C_2H_5; A = $Co_3(CO)_{10}$, R = CH_3; A = $FeCo_3(CO)_{12}$, R = CH_3, C_2H_5, n-C_3H_7).

The study of the reactions of dinitrogen complexes with transition metal hydrides seems intriguing in the search for catalytic systems to facilitate the reduction of dinitrogen by dihydrogen under mild conditions. We recently reported the formation of ammonia and hydrazine from cis-$[W(N_2)_2(PMe_2Ph)_4]$ by means of hydridometal carbonyls, $H_2Fe(CO)_4$ or $HFeCo_3(CO)_{12}$.[1] The yields of the nitrogen hydrides increased under hydrogen atmosphere. The present communication reports the synthesis of alkoxy-hydrazido(2-) complexes by the treatment of trans-$[W(N_2)_2(dpe)_2]$ 1 with hydridometal carbonyls, $HCo(CO)_4$ or $HFeCo_3(CO)_{12}$ in the presence of an alcohol. In the protonation reactions of dinitrogen complexes of molybdenum and tungsten, alcohols played a significant role.[2,3] The isolation of the present complexes supports the assumption that the protons in the hydrazido(2-) ligand come from the hydridometal carbonyl and the alcohol.

Complex 1 and excess methanol were mixed with a hexane solution of 6 equivalents of $HCo(CO)_4$ prepared under carbon monoxide by the method in literature[4] and stirred for 20 h at -20 °C under nitrogen. The color of the suspension turned from orange to light yellow. After the solvent and excess $HCo(CO)_4$ were evaporated in vacuo below 0 °C, the residue was washed with methanol and hexane, and recrystallized from dichloromethane-methanol to give yellow crystals, $[W(OCH_3)(NNH_2)(dpe)_2]^+[Co(CO)_4]^-$ 2 (yield 51%). Ether was added to the washing solution and the mixture was kept for a day to afford dark green crystals, $[W(OCH_3)(NNH_2)(dpe)_2]^+[Co_3(CO)_{10}]^-$ 4 (yield 7%). The ethoxy-hydrazido(2-) complex $[W(OC_2H_5)(NNH_2)(dpe)_2]^+[Co(CO)_4]^-$ 3 was obtained by the reaction of 1 with a hexane solution of $HCo(CO)_4$ in the presence of ethanol in toluene at -20 °C for 44 h (yield 26%).

$$[W(N_2)_2(dpe)_2] + HCo(CO)_4 + ROH \xrightarrow[\text{hexane + toluene}]{\text{-20 °C}} [W(OR)(NNH_2)(dpe)_2]^+[Co(CO)_4]^-$$

R = CH_3 2, C_2H_5 3

The reaction of complex 1 with $HFeCo_3(CO)_{12}$ and excess methanol in toluene under nitrogen at room temperature for 6 h afforded black crystals $[W(OCH_3)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ 5 (yield 77%). With ethanol or 1-propanol, similar complexes containing ethoxy 6 (yield 76%) or 1-propoxy 7 (yield 59%) ligand formed.

$$[W(N_2)_2(dpe)_2] + HFeCo_3(CO)_{12} + ROH \xrightarrow[\text{toluene}]{\text{r.t.}} [W(OR)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$$

R = CH_3 5, C_2H_5 6, n-C_3H_7 7

The complexes 2 and 3 containing $[Co(CO)_4]^-$ are rather air-sensitive, whereas 5, 6 and 7 containing $[FeCo_3(CO)_{12}]^-$ are quite air-stable in solid states. Spectroscopic data of 2 - 7 in the Table are consistent with their formulation as alkoxy-hydrazido(2-) complexes. The IR spectrum of 2 indicates a very strong peak at 1886 cm^{-1} assignable to νC≡O and a strong peak at 558 cm^{-1} assignable to νCo-(CO). These wave numbers are near those of solid salts of $[Co(CO)_4]^-$ [5] and suggest the presence of an anionic $[Co(CO)_4]^-$ in the complex 2. The νC≡O frequencies of $[Co_3(CO)_{10}]^-$ in 4 and of $[FeCo_3(CO)_{12}]^-$ in 5 - 7 are also shown in the Table.

Full characterization including X-ray crystal structure determination of these complexes is now in progress.

Table. Spectroscopic Data* of Alkoxy-hydrazido(2-) Complexes $[W(OR)(NNH_2)(dpe)_2]^+[A]^-$

Complex	R	A	IR Data /cm^{-1} [a] νN-H	νO-C	νC≡O	^{1}H NMR Data[b] δNNH_2 /ppm
2	CH_3	$Co(CO)_4$	3346, 3260	1119	2000 w, 1886 vs	3.45
3	C_2H_5	$Co(CO)_4$	3362, 3268	1065	2000 w, 1886 vs	3.33
4	CH_3	$Co_3(CO)_{10}$	3374, 3264	1120	2046 w, 1975 vs, 1954 sh, 1886 m, 1771 w, 1731 m	3.22
5	CH_3	$FeCo_3(CO)_{12}$	3352, 3264	1144	2052 w, 1990 vs, 1960 sh, 1924 s, 1856 w, 1806 s	3.36
6	C_2H_5	$FeCo_3(CO)_{12}$	3338, 3282	1073	2069 w, 2000 vs, 1970 sh, 1927 s, 1860 w, 1810 s	3.28
7	n-C_3H_7	$FeCo_3(CO)_{12}$	3361, 3270	1084	2070 w, 1996 vs, 1969 sh, 1925 s, 1859 w, 1816 s	3.26

* The elemental analyses of the complexes gave satisfactory values. [a] KBr disk. [b] CD_2Cl_2 solution.

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