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Improved synthesis of the radical source bis[2,2,6,6-tetramethylpiperidyl-(1)]-disulfide and photoinduced reactions with $M_2(CO)_{10}$ (M = Mn, Re)

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

Abstract

An improved synthesis of bis[2,2,6,6-tetramethylpiperidyl-(1)]-disulfide ($(tmps)_2$) in moderate yield is reported. Reaction of *N*-(trimethylsilyl)-imidazole with S_2Cl_2 gives *N,N′*-dithiobisimidazole and trimethylsilylchloride. The disulfide undergoes exchange of the heterocycle wth 2,2,6,6-tetramethylpiperidine and yields bis[2,2,6,6-tetramethylpiperidyl-(1)]-disulfide and imidazole. This synthesis offers the advantage that only traces of the bis[2,2,6,6-tetramethylpiperidyl-(1)]-trisulfide are produced. The synthesis and spectroscopic properties of the dimeric compounds $[M(CO)_4tmps]_2$ (M = Mn, Re) obtained by UV irradiation of a mixture of $(tmps)_2$ with $M_2(CO)_{10}$ (M = Mn, Re) is described. © 2001 Elsevier Science B.V. All rights reserved.

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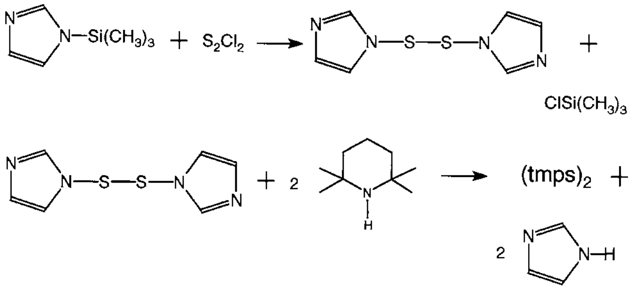
1. Introduction

The nitroxyl radical 2,2,6,6-tetramethylpiperidin-1-oxyl (tmpo) is a powerful paramagnetic ligand when studying magnetic interactions between metal centers and ligands [1], in the design of new magnetic materials [2] or as catalyst for selective oxidations [3]. We have shown that tmpo is also a valuable spin scavenger of metal carbonyl radicals generating diamagnetic electron deficient complexes like $V(CO)_3tmpo$, $Mn(CO)_3tmpo$ and $Co(CO)_2tmpo$, containing a η^2-bonded tmpo ligand [4]. A metal (^{51}V, ^{55}Mn, ^{59}Co) NMR investigation revealed that these strained three-membered metallacycles exhibit extremely low metal shieldings [5].

A new synthetic application of tmpo is the oxo transfer to $Co_2(CO)_8$, generating an oxo-centered tetrahedral cluster $Co_4O(OOCNC_9H_{18})_6$ reported recently by us [6]. Surprisingly, the reaction of $[Co_2(CO)_8]$ in the presence of a four-fold excess of tmpo promotes the generation of the blue carbamato complex $Co_4O(OOCNC_9H_{18})_6$ in a few minutes. Even though the mechanism of formation of this complex is not completely understood, the synthetic methodology shown in this work opens a new and accessible synthetic route to the obtaining of clusters with the general formulation $[M_4(\mu_4\text{-}O)]^{6+}$. Such type of clusters, with a four-coordinate oxygen atom occupying the center of a tetrahedron of divalent metal atoms, is a classical structure in inorganic chemistry. As we wished to extend this valuable synthetic oxo transfer to sulfur, we have been searching for a synthetic entry to thionitroxyl radicals. We selected $(tmps)_2$ as the source of NS radicals.



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2. Results and discussion

The sulfur analogue of tmpo, the thionitroxide $(tmps)_2$, was described first by J.E. Bennnett et.al. in 1967 [7]. They obtained the disulfide $(tmps)_2$ from the corresponding piperidine and sulfur dichloride (SCl_2) in low yield (16%).

The disulfide $(tmps)_2$ is stable at room temperature but when heated as a solid or in solution it dissociates at 90–200°C into thionitroxyl radicals. A three-line esr signal is observed indicating that the homolytic fission of the S–S bond takes place. The intensity of the esr signal increased and decreased reversibly, as the temperature was raised or lowered over a limited range.

The synthesis of $(tmps)_2$ according to the method of J.E. Bennett has some disadvantages, such as low yield (16% calc.on tetramethylpiperidine) and considerable amounts of the corresponding trisulfide that are difficult to separate.

We developed a two-step synthesis of $(tmps)_2$. Reaction of *N*-(trimethylsilyl)-imidazole with freshly distilled S_2Cl_2 in benzene gives *N*,*N*′-dithiobisimidazole and trimethylsilylchloride. The disulfide undergoes exchange of the heterocycle wth 2,2,6,6-tetramethylpiperidine and yields bis[2,2,6,6-tetramethylpiperidyl-(1)]-disulfide and imidazole. This synthesis offers the advantage that only traces of the bis[2,2,6,6-tetramethylpiperidyl-(1)]-trisulfide are produced (see Eq. (1)).

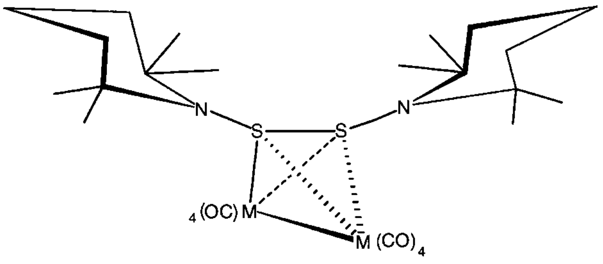

Fig. 1. Suggested structure of $[M(CO)_4tmps]_2$.

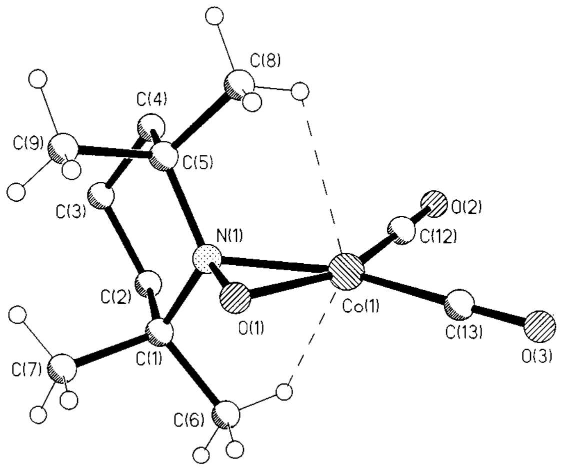

Fig. 2. Molecular structure of $[CO(CO)_2tmpo]$.

We wish to report the synthesis of diamagnetic $[M(CO)_4tmps]_2$ (M = Mn, Re), both coordinatively saturated compounds prepared by photolysis of the dimeric metal carbonyls $M_2(CO)_{10}$ (M = Mn, Re) in the presence of the disulfide $(tmps)_2$. The photogenerated reactive $M(CO)_5$ and monomeric tmps radicals recombine by loss of CO, affording good yields (> 50%) of dimeric compounds of the type $[M(CO)_4tmps]_2$ (M = Mn, Re). Surprisingly, none of the expected pentacoordinated complexes, like $Mn(CO)_3tmpo$ or $V(CO)_3tmpo$ [4], were obtained.

An explanation for this unexpected behaviour could be the high recombination rate of the NS radicals favouring dimeric complexes with a disulfide bridge. Further photolysis and decarbonylation of the compounds $[M(CO)_4tmps]_2$ in order to obtain tetrameric clusters, like $[Mn(CO)_3SC_6H_5]_4$ [8], proved to be unsuccessful. The steric requirements of such a 'Mn_4S_4' cubane presumably do not allow decarbonylation.

The characterization of $[M(CO)_4tmps]_2$ (M = Mn, Re) was by infrared and elemental analysis. The infrared spectra exhibit four active carbonyl stretching modes characteristic for a $M(CO)_4$ group. Nearly equal intensities of the IR peaks indicate 90° angles between the CO ligands. In the mass spectra only monomeric fragment ions are observed. In accordance with the spectroscopic data and the known structure of $[Mn(CO)_4SR]_2$ [8 and lit. cited therein] we suggest for $[M(CO)_4tmps]_2$ (M = Mn, Re) the tetrahedral structure illustrated in Fig. 1.

Photolysis at r.t. of the metal carbonyl $Co_2(CO)_8$ in presence of the disulfide $(tmps)_2$ gave a very sensitive, non-isolatable compound. When monitoring the reaction by infrared spectroscopy we observed formation of a new Co compound with three CO stretching modes (2043s, 2012s, 1935s cm^{-1}, *n*-pentane). But during evaporation of the solvent in vacuo of the deep red solution decomposition occurs and only amorphous cobalt was obtained. Repeated photolysis at 0°C and variation of the solvent showed no success.

In order to elucidate the products obtained during photolysis of $Co_2(CO)_8$ with tmpo or of $Co_2(CO)_8$ with the disulfide $(tmps)_2$, we have re-prepared $[Co(CO)_2tmpo]$ and characterized it by NMR (^1H, ^{13}C, ^{17}O).

The molecular structure of complex $[Co(CO)_2tmpo]$ was determined by single crystal X-ray diffraction spectrometry showing that the Co^I atom is in a planar coordination with the two carbonyls and the O–N group of the tmpo ligand (see Fig. 2).

No addition of CO, PR_3 or H_2 to $[Co(CO)_2tmpo]$ takes place since the two methyl groups of the coordinated tmpo protect the Co-atom from above and below the planar molecular arrangement.

The ^1H-NMR of the hydroxylamido compound $[Co(CO)_2tmpo]$ shows diastereotopic protons of the different methyl groups located at 0.98 and 1.26 ppm [9]. In the ^{13}C-NMR of [Co(CO)$_2$tmpo] the three resonances of the piperidin carbon atoms and two diastereotopic methyl groups are present. The assignement of the ^{13}C signals has been verified by a DEPT experiment (see Section 3). The resonances of the CO ligands are not visible due to the large quadrupole of the Co atom while the ^{17}O-NMR spectrum shows two separated signals for the different CO groups. The distance from the Co atom and the next located H of a methyl group is 2.51 and 2.47, demonstrating the lack of agostic interactions between the Co ion and H.

The ^{1}H-NMR of the corresponding solutions obtained by photolsis of (tmps)$_2$ and Co$_2$(CO)$_8$ failed since only broad resonances were obtained, indicating that the product is paramagnetic or that radical impurities are present.

3. Experimental

3.1. Synthesis of (tmps)$_2$

S$_2$Cl$_2$ (6.75 g, 50 mmol) was placed in a 250 ml Schlenk flask that was thoroughly dried, flushed repetedly with argon and equipped with a magnetic stirbar. To this flask 25 ml of dry benzene was added. A solution of *N*-(trimethylsilyl)-imidazole (14.0 g, 100 mmol in 25 ml dry benzene) was added dropwise (3 h). After srirring the solution for another 2 h the solvent and trimethylsilylchloride were removed under vacuum. The product was dried for another hour (10^{-2} mmHg) in order to remove traces of trimethylsilylchloride. The colorless crystalline disulfide was dissolved in dry 25 ml benzene and 2,2,6,6-tetramethylpiperidine (14.1 g, 100 mmol) was added. The solution was stirred for 5 h at room temperature and the solvent then removed. The residue was dissolved in 150 ml dry *n*-pentane and filtered under argon in order to remove the imidazole. Recrystallization twice from dry ethanol gave (tmps)$_2$ (10.7 g, yield 62%, m.p. 82–84°C).

No trisulfide could be detected by mass spectrometry. The S$_2$Cl$_2$ must be freshly distilled, otherwise tri- and tetra-sulfide is formed.

3.2. Synthesis of [Mn(CO)$_4$tmps]$_2$

A Schlenk tube charged with 293 mg (0.75 mmol) Mn$_2$(CO)$_{10}$ and 258 mg (0.75 mmol) (tmps)$_2$ in 50 ml *n*-pentane was irradiated at 0°C with a UV lamp (Hanau 150 W) for 90 min. During photoreaction the initially brown solution turned deep red. After evaporation of the solvent and separation of the unreacted Mn$_2$(CO)$_{10}$ by sublimation, the solid was redisolved in 5 ml dry *n*-pentane and filtered under argon to remove solids.

Deep red crystals, m.p. 87.0°C (decomp.). IR: 2060s, 2010s, 1985s, 1950s; *n*-pentane. Anal. Calc: C, 46.02; H, 5.35; N, 4.13; O, 18.86. Found: C, 46.29; H, 6.01; N, 4.17; O, 18.66. Yield 50%.

3.3. Synthesis of [Re(CO)$_4$tmps]$_2$

A Schlenk tube charged with 456 mg (0.70 mmol) Re$_2$(CO)$_{10}$ and 241 mg (0.70 mmol) (tmps)$_2$ in 20 ml *n*-pentane was irradiated at 0°C with a UV lamp (Hanau 150 W) for 180 min. During photoreaction the initially brown solution turned orange. After evaporation of the solvent the red solid was washed with *n*-pentane and ether, redisolved in 5 ml dry *n*-pentane and filtered under argon to remove solids.

Red crystals, m.p. 160.0°C (decomp.). IR: 2080s, 2000s, 1975s, 1940s, *n*-pentane. Anal. Calc: C, 33.18; H, 3.86; N, 2.98; O, 13.60. Found: C, 31.42; H, 3.46; N, 2.49; O, 15.85. Yield 35%.

3.4. Synthesis of [Co(CO)$_2$tmpo]

A Schlenk tube charged with 342 mg (1.0 mmol) Co$_2$(CO)$_8$ and 312 mg (2.0 mmol) 2,2,6,6-tetramethylpiperidin-1-oxyl in 40 ml n-pentane was irradiated at r.t. with a UV lamp (Hanau 150 W) for 30 min. During photoreaction the initially brown solution turned deep red. Workup: vacuum sublimation (10^{-2} mmHg, 30°C) gave traces of unreacted tmpo,vacuum sublimation of the residue (10^{-2} mmHg, 40°C) gave suitable single crystals (yield $>$ 80%).

Red brown crystals, m.p. 70°C. ^{1}H-NMR (C$_6$D$_6$): δ 1.22. (6H, s); 0.92 (6H, s); 1.35, 1.30, 1.10, 1.06 (unresolved multiplet). ^{13}C-NMR (C$_6$D$_6$): δ 65.5(s) C(1) and C(5), 37.9(s) C(2) and C(4), 32.9(s) (Me), 23.9(s) (Me), 16.7(s) C(3); carbon atoms are denoted as shown in Fig. 2. DEPT experiments (135) show methyl groups positive.

^{17}O-NMR (in benzene with C$_6$D$_6$): 374 ppm, 368 ppm with reference to $H_2^{17}O$. All manipulations were carried out under dry argon. Solvents were distilled from sodium wire under argon. Ultraviolet irradiations were performed with a high pressure mercury lamp (Hanau 150 W) in a Schlenk tube equipped with a pressure valve.

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