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Facile and highly efficient light-induced PR_3/CO ligand exchange: A novel approach to the synthesis of $[(\mu-SCH_2N^nPrCH_2S)Fe_2(CO)_4(PR_3)_2]$

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Abstract

A straightforward and efficient transformation of the Fe–S complex $[(\mu$ -SCH₂N^{*n*}PrCH₂S)Fe₂(CO)₆] to its double phosphine coordinated analogues $[(\mu$ -SCH₂N^{*n*}PrCH₂S)Fe₂(CO)₄(PR₃)₂] (R = Ph, Me) is described. The single crystal structure of the PPh₃-disubstituted complex $[(\mu$ -SCH₂N^{*n*}PrCH₂S)Fe₂(CO)₄(Ph₃P)₂] (**3**) showed that both of the phosphine ligands take an apical/apical instead of a basal/basal or an apical/basal configuration.

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1. Introduction

Dinuclear butterfly Fe–S complexes $[Fe_2(\mu$ -S-R-S)- $(CO)_6]$ (R = $-(CH_2)_{3-}$, $-CH_2NR'CH_2-$) have been extensively studied as models for the active site of Fe-only hydrogenases [1]. One significant type of model complex is the bisphosphine coordinated derivative. The phosphine ligands have been found to increase protonation capability at the Fe–Fe moiety and therefore favour molecular hydrogen formation. Although the carbonyl displacement reactions between $[Fe_2(\mu$ -S-R-S)(CO)_6] and tertiary phosphines (PMe₃, PPhMe₂, P(OMe)₃, PPh₃) have been extensively studied since the 1970s, the preparation of the bis-phosphine coordinated product, particularly the bistriphenylphosphine, remains difficult. While the preparation of bis-phosphine complexes of PMe₃ proceeds smoothly in

the case of $[(\mu-SCH_2NR'CH_2S)Fe_2(CO)_4L_2]$ (L = PMe₃, R' = benzyl) complex [2], the prior preparation of [(μ - $SCH_2NR'CH_2S)Fe_2(CO)_4L_2$] (L = PMe₃, R' = p-nitrophenyl) complex [3] involved in the reaction of the Fe_2S_2 hexacarbonyl model complex with a large excess of phosphine in heated toluene. The propanedithiolato-bridged dinuclear analogue $[(\mu-PDT)Fe_2(CO)_4L_2] \quad (L = PR_3)$ $(PDT = propanedithiolate, -SCH_2CH_2CH_2S-)$ was also prepared in similar manner [4–7]. So far, no reactions have been reported by using sunlight to induce direct CO-substitution by phosphine. This paper describes a novel and convenient protocol, employing light-induced ligand exchange for the synthesis of the PR₃-disubstituted model complexes $[(\mu-SCH_2N^nPrCH_2S)Fe_2(CO)_4(L)_2](L = PMe_3, PPh_3).$

2. Results and discussion

2.1. Synthesis

We chose azadithiolate containing Fe_2S_2 system [{(μ -SCH₂N(CH₂CH₂CH₃)CH₂S)}Fe₂(CO)₆] (1) as the

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substrate for our studies. The propyl group was used as the N-substituent because of its simplicity and electron-releasing ability [8]. As expected, the PPh₃-monosubstituted complex 2 could be obtained in good yield by the reaction of 1 with 1 equiv. of PPh₃ and 1 equiv. of Me₃NO. As an oxidative decarbonylation reagent in the CO/phosphine substitution [9], Me₃NO can transfer an oxygen to carbonyl and accelerates the substitution reaction for the type of $[(\mu$ -SCH₂NRCH₂S)Fe₂(CO)₅L] (L = phosphine ligand). However, further conversion to the bis-PPh₃-substituted complex 3 was difficult even if excessive PPh₃ and Me₃NO were involved, perhaps because of the weak oxidation ability of the latter compared to [FeCp₂]PF₆ in MeNO₂ [10,11]. When the reaction of 1 with only 2 equiv. of PPh₃ was carried out under sunlight in the presence of Me₃NO, the PPh₃/CO exchange proceeded quite smoothly and complex 1 was transformed into complex 3 in excellent yield (Scheme 1). It turned out both sunlight and Me₃NO were essential for this reaction. In the absence of sunlight, it was rather difficult to obtain the disubstituted complex 3 even at high temperature with an excess of PPh₃. In contrast, in the absence of Me₃NO but under sunlight, the substitution still occurred affording a mixture of the monoand disubstituted PPh₃ complexes, but the yield was relatively low, ca. 5% mono- and 10% disubstituted product, respectively. It was also evident that complex 2 was the intermediate in the formation of a bis-PPh₃-substituted complex 3. Similar results were obtained with PMe_3 to give $[\{(\mu-SCH_2N(CH_2CH_2CH_3)CH_2S)\}Fe_2(CO)_5(PMe_3)]$ (4) and $[{(\mu-SCH_2N(CH_2CH_2CH_3)CH_2S)}Fe_2(CO)_4(PMe_3)_2]$

Table 1 The control experiments for the synthesis of PR_3 -disubstituted Fe_2S_2 complexes^a

Complexes	Me ₃ NO only ^b (%)	Light only (%)	Me ₃ NO/light ^b (%)
3	<1	10	95
5	30	21	90
7	<1	<1	92
8	11	9	87

^a The mole ratio of PR_3/Fe_2S_2 is 2:1.

^b The mole ratio of Me₃NO/Fe₂S₂ is 1:1.

(5), in yields of 95% and 90%, respectively. Unfortunately, we did not obtain complexes 4 and 5 in crystalline form because of their oily state. These results could be further extended to PDT analogues. As expected, the conversions from the reported complex 6 to the known complexes 7 and $\mathbf{8}$ were easily realized in yields of 92% and 87%, respectively; especially for complex 7, much higher than the reported yield of 20% [7]. Control experiments were also performed to show the efficiency of combined using of Me₃NO and light (Table 1). Under the action of Me₃NO $(Me_3NO/Fe_2S_2 = 1:1)$, the bis-PPh₃ substituted complexes can barely be detected. When 10-folds of Me₃NO was used, the bis-PPh₃ substituted complexes 3 and 7 could be obtained but still in a very low yield (ca. 10%). In the case of bis-PMe₃ coordinated complexes 5 and 8, the relatively improved yields of 30% and 11% are probably due to the more strong electron-donating ability of PMe₃ compared with PPh₃. When such reaction was performed by irradiation, it did not show an increasing trend for yields. How-



Scheme 1. Synthetic route for the PR3-disubstituted Fe-S complexes.

ever, all target bisphosphine products could be obtained in good yields with the combined use of Me₃NO and light.

2.2. Characterization

All of the new complexes had been characterized by their ¹H NMR and mass spectra. The most intense peaks were observed for **2** and **3** in the mass spectra at m/z 664 and 898 respectively, corresponding to $[M+H]^+$ (positive mode). In order to have a better understanding of the reaction process, the ³¹P NMR spectroscopic changes were recorded (Fig. 1). The ³¹P NMR signals observed were first -5.5 ppm (PPh₃), then 65.6 ppm (PPh₃-monosubstituted complex **2**) and finally 62.7 ppm (PPh₃-disubstituted complex **3**). After 10 min, the PPh₃-monosubstituted complex **2** was observed with some PPh₃ left. When the reaction mixture was kept in the dark, the ³¹P NMR spectrum remained unchanged for a further 20 min or even longer. However, if the reaction mixture was then irradiated with visible light, most of the PPh₃ had coordinated to iron within 30 min. The weak signal at 43.1 ppm was due to the S = PPh₃ which



Fig. 1. Time dependence of 31 P NMR spectra of 1+PPh₃ (molar ratio: 1:2): (a) SPPh₃ (43.1 ppm) and PPh₃ (before reaction), (b) at room temperature without light and (c) under sunlight irradiation.

has been characterized by single crystal X-ray analysis. The ¹H NMR signals for most $CH_3CH_2CH_2$ and $P(CH_3)_3$ groups are reported as singlets usually attribute to the intrinsic property of the iron-containing compounds.

Some control experiments at an early stage clarified the formation of phosphine sulfide in the reaction of complexes **1** or **6** with phosphine ligand (Scheme 2). Two requisite conditions were the presence of the bridge nitrogen and Me₃NO, since the reaction of **6** failed to give phosphine sulfide. The mechanism might possibly involve the nucleophilic attack by a bridging sulfur atom or the direct oxidation of iron (I) by Me₃NO, followed by reaction of Ph₃P with any sulfur formed.

The coordination configuration of diphosphine complex had been structurally characterized (Fig. 2), and compared to the structures of its analogues $[Fe_2(\mu-S-R-S)(CO)_4(L)_2]$ $(L = PMe_3, \text{ or } PMe_2Ph)$ [7–12]. The single crystal X-ray analysis showed that the PPh₃-disubstituted complex **3** possesses an *ap/ap* (apical/apical, *trans* position relative to the



Fig. 2. ORTEP view of $[{(\mu-SCH_2N''PrCH_2S)}Fe_2(CO)_4(PPh_3)_2]$ (3) with 30% ellipsoids. Selected bond distances (Å) and angles (deg): Fe(1)–Fe(2) 2.5181(12), Fe(1)–S(1) 2.269(2), Fe(1)–S(2) 2.2662(17), Fe(1)–P(2) 2.2459(17), Fe(1)–S(1)–Fe(2) 67.36(6), Fe(1)–S(2)–Fe(2) 67.27(5), P(2)–Fe(1)–Fe(2) 156.92(6).



Scheme 2. Different substrates and reaction conditions relating to the formation of Ph₃PS.

Fe-Fe bond) coordination configuration, which was identical to that of the complexes containing the large isocyanide ligand *t*BuNC [13] and PMe₂Ph-disubstituted complex [7]. but in contrast to the transoid ba/ba (basal/basal, cis to the Fe–Fe bond) configuration of $[(\mu-PDT)Fe_2(CO)_4(PMe_3)_2]$ [12] and $[(\mu-PDT)Fe_2(CO)_4(PTA)_2]$ [14] (PTA = 1,3,5-triaza-7-phosphaadamantane). This feature showed that for larger tertiary phosphine ligands, a ba/ba or an ap/ba configuration should be more sterically crowded than an ap/apconfiguration. The newly reported PMe₃-disubstituted derivatives $[{(\mu-SCH_2N(R')CH_2S)}Fe_2(CO)_4(PMe_3)_2]$ $(\mathbf{R}' = p$ -nitrophenyl or benzyl) usually take a *ba/ba* or an ap/ba configurations [2,3]. However, the coordination configurations of other PR₃-disubstituted complexes [(µ- $SCH_2N(R')CH_2S)Fe_2(CO)_4L_2$ (L = PMe_2Ph, PPh₃) were unknown prior to the preparation of the PPh3-disubstituted derivative reported here.

3. Conclusion

In summary, PR₃-disubstituted azadithiolato diiron species were prepared in excellent yield *via* the direct irradiation in the presence of Me₃NO, which provided a new and efficient access for synthesizing the disubstituted phosphine Fe-only hydrogenases model complexes. The conversion showed excellent yield with remarkably site-selective properties, with the PPh₃ taking uniquely ap/ap configuration. The results may be biosynthetically relevant, especially in view of the importance of its site-selectivity and further protonation.

4. Experimental

4.1. General considerations

All reactions and operations related to organometallic complexes were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and distilled prior to use according to the standard methods. Commercially available chemicals, including n-propylamine, paraformaldehyde, trimethylamine oxide and triphenylphosphine were used without further purification. The reagents LiEt₃BH, triflic acid and trimethylphosphine (1 M in THF) were purchased from Aldrich. Infrared spectra were recorded on a JASCO FT/ IR 430 spectrophotometer. NMR spectra were collected on a Varian INOVA 400NMR spectrometer at 400 MHz (¹H) and at 161 MHz (³¹P). Mass spectra were recorded on an HP1100 MSD instrument. Elemental analyses were performed on a CARLO ERBA MOD-1106 elemental analyzer.

4.2. $[{(\mu-SCH_2N(CH_2CH_2CH_3)CH_2S)}Fe_2(CO)_5-(PPh_3)]$ (2)

A solution of 1 (43 mg, 0.1 mmol) in CH_3CN (20 mL) was added dropwise to a CH_3CN (3 mL) solution of

 $Me_3NO \cdot 2H_2O$ (11 mg, 0.1 mmol) at room temperature. Then a CH₂Cl₂ (5 mL) solution of PPh₃ (26 mg, 0.1 mmol) was added to the above solution during 10 min. After another 30 min, the solvent was removed and the residue was purified by silica gel chromatography (CH₂Cl₂/hexane 1:2) to give two components: complex 2 (64 mg, 97%) as a red solid: mp 78–80 °C. ¹H NMR (CD₃COCD₃): δ (ppm) 0.61 (t, J = 7.2 Hz, 3H, CH_3), 1.01–1.07 (m, 2H, CH₃CH₂CH₂), 1.29 (s, b, 2H, CH₃CH₂CH₂N), 2.39 (d, J = 11.2 Hz, 2H, NCH₂S), 2.92 (d, J = 14.4 Hz, 2H, NCH₂S), 7.28–7.32 (m, 3H, Ph), 7.39–7.40 (m, 6H, Ph), 7.54–7.55 (m, 3H, Ph), 7.70–7.74 (m, 3H, Ph). ³¹P NMR (CH₂Cl₂): δ (ppm) 65.60 (s). IR (KBr): ν(CO) 2041, 1989, 1961, 1930 cm⁻¹. MS (API-ES): m/z 664.0 [M+H]⁺. Elemental Anal. Calc. for C₂₈H₂₆Fe₂NO₅PS₂: C, 50.70; H, 3.95; N, 2.11. Found: C, 50.92; H, 4.14; N, 2.33%. SPPh₃ (1.5 mg, 5%) as a white solid: mp 160–162 °C (lit. [15] mp 162–164 °C). ¹H NMR (CDCl₃): δ (ppm) 7.41–7.45 (m, 6H, Ph), 7.48–7.50 (m, 3H, Ph), 7.69–7.74 (m, 6H, Ph). ³¹P NMR (CH₂Cl₂): δ (ppm) 43.1 (s).

4.3. $[{(\mu-SCH_2N(CH_2CH_2CH_3)CH_2S)}Fe_2(CO)_4-(PPh_3)_2]$ (3)

This complex was prepared by a similar procedure, with 2 equiv. PPh₃ except that the reaction was carried out under sunlight or irradiated with a 500 W Xe lamp. After 30 min reaction time, the solvent was removed and the residue was purified by silica gel chromatography with CH₂Cl₂/hexane (1:2) to give complex **3** (84 mg, 95%) as a red solid: mp 120 °C (dec.). ¹H NMR (CD₃COCD₃): δ 0.88 (t, J = 6.8 Hz, 3H, CH₃), 1.07–1.10 (m, 2H, CH₃CH₂CH₂), 1.76 (s, 2H, CH₃CH₂CH₂N), 2.95 (s, 4H, NCH₂S), 7.48–7.49 (m, 18H, Ph), 7.69–7.73 (m, 12H, Ph) ppm. ³¹P NMR (CH₂Cl₂): δ 62.67 (s) ppm. IR (KBr): ν (CO) 1995, 1952 and 1932 cm⁻¹. MS (API-ES): m/z 898.0 [M+H]⁺. Elemental Anal. Calc. for C₄₅H₄₁Fe₂NO₄P₂S₂: C, 60.22; H, 4.60; N, 1.56. Found: C, 60.45; H, 4.70; N, 1.78%.

4.4. $[{(\mu-SCH_2N(CH_2CH_2CH_3)CH_2S)}Fe_2(CO)_5-(PMe_3)]$ (4)

A solution of 1 (43 mg, 0.1 mmol) in CH₃CN (20 mL) was added dropwise to a CH₃CN (3 mL) solution of Me₃NO · 2H₂O (11 mg, 0.1 mmol) at room temperature. Then a 1 M THF solution of PMe₃ (0.1 mL, 0.1 mmol) was added to the above solution during 10 min. After 30 min, the solvent was removed and the residue was purified by silica gel chromatography with CH₂Cl₂/hexane (1:2) to give complex **4** (46 mg, 95%) as red oil: ¹H NMR (CDCl₃): δ (ppm) 0.80 (s, 3H, CH₃), 1.30 (s, 2H, CH₃CH₂CH₂CH₂N), 3.46 (s, 4H, 2×NCH₂S). ³¹P NMR (CDCl₃): δ (ppm) 25.1 (d). IR (CHCl₃): ν (CO) 2035, 1978, 1942, 1908 cm⁻¹. Elemental Anal. Calc. for C₁₃H₂₀Fe₂NO₅PS₂: C, 32.73; H, 4.23; N, 2.94. Found: C, 33.10; H, 4.44; N, 2.86%.

4.5. $[{(\mu-SCH_2N(CH_2CH_2CH_3)CH_2S)}Fe_2(CO)_4-(PMe_3)_2]$ (5)

This complex was prepared by a similar procedure, with 2 equiv. PMe₃ except that the reaction was carried out under sunlight or irradiated with a 500 W Xe lamp. After 30 min reaction time, the solvent was removed and the residue was purified by silica gel chromatography with CH₂Cl₂/hexane/Et₃N (100:200:1) to give a red oily complex **5** (47 mg, 90%). ¹H NMR (CDCl₃): δ (ppm) 0.74 (s, 3H, CH₃), 1.93 (s, 2H, CH₃CH₂CH₂N), 3.14 (s, 4H, 2×NCH₂S). ³¹P NMR (CD₃CN): δ (ppm) 23.12 (s). IR (CHCl₃): ν (CO) 1998, 1979, 1940, 1898 cm⁻¹. Elemental Anal. Calc. for C₁₅H₂₉Fe₂NO₄P₂S₂: C, 34.31; H, 5.57; N, 2.67. Found: C, 34.51; H, 5.25; N, 2.39%.

4.6. Crystal data for 3 and SPPh₃

Single crystal X-ray diffraction patterns were recorded with an Oxford Diffraction Excalibur diffractometer equipped with a sapphire-3 CCD on a Mo-radiation source $(\lambda = 0.71073 \text{ Å})$ with ω -scans of at different ϕ to fill Ewald sphere. The sample-detector distance was 50 mm. The maximum $2\theta \approx 63^{\circ}$. The crystal structure was solved by SHELXL-97.

Crystal data for 3: triclinic, $C_{45}H_{41}Fe_2NO4P_2S_2$, M = 897.55, space group: $P\bar{1}$, a = 10.3380(19) Å, b = 10.551(2) Å, c = 22.833(4) Å, $\alpha = 90.132(2)^{\circ}$, $\beta = 99.352(3)^{\circ}$, $\gamma = 119.182(2)^{\circ}$, V = 2135.9(7) Å³, Z = 2, T = 273 K, $\mu = 0.895$ mm⁻¹, 4228 reflection observed, $R_1 = 0.0620$ and $wR_2 = 0.1581$. Crystal data for SPPh₃: monoclinic, $C_{18}H_{15}P_1S_1$, M = 294.33, space group: $P\bar{2}(1)/c$, a = 18.320 (3) Å, b = 9.6370(14) Å, c = 18.007(3) Å, $\alpha = 90.00^{\circ}$, $\beta = 105.944(3)^{\circ}$, $\gamma = 90.00^{\circ}$, V = 3056.8(8) Å³, Z = 8, T = 273 K, $\mu = 0.303$ mm⁻¹, 1970 reflection observed, $R_1 = 0.0765$ and $wR_2 = 0.1473$.

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Appendix A. Supplementary material

CCDC 299478 and 288105 contain the supplementary crystallographic data for **3** and SPPh₃. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.12.009.

References

- [1] (a) D.J. Evans, C.J. Picket, Chem. Soc. Rev. 32 (2003) 268;
 (b) I.P. Georgakaki, L.M. Thomson, E.J. Lyon, M.B. Hall, M.Y. Darensbourg, Coord. Chem. Rev. 238–239 (2003) 255;
 (c) T.B. Rauchfuss, Inorg. Chem. 43 (2004) 14;
 (d) L. Sun, B. Åkermark, S. Ott, Coord. Chem. Rev. 249 (2005) 1653.
- [2] L. Schwartz, G. Eilers, L. Eriksson, A. Gogoll, R. Lomoth, S. Ott, Chem. Commun. (2006) 520.
- [3] W. Dong, M. Wang, X. Liu, K. Jin, G. Li, F. Wang, L. Sun, Chem. Commun. (2006) 305.
- [4] I.P. Georgakaki, M.L. Miller, M.Y. Darensbourg, Inorg. Chem. 42 (2003) 2489.
- [5] M.M. Hasan, M.B. Hursthouse, S.E. Habir, K.M.A. Malik, Polyhedron 20 (2001) 97.
- [6] F. Gloaguen, J.D. Lawrence, T.B. Rauchfuss, J. Am. Chem. Soc. 123 (2001) 9476.
- [7] P. Li, M. Wang, C. He, G. Li, X. Liu, C. Chen, B. Åkermark, L. Sun, Eur. J. Inorg. Chem. (2005) 2506.
- [8] W. Gao, J. Liu, C. Ma, L. Weng, K. Jin, C. Chen, B. Åkermark, L. Sun, Inorg. Chim. Acta 359 (2006) 1071.
- [9] F. Gloaguen, J.D. Lawrence, M. Schmidt, S.R. Wilson, T.B. Rauchfuss, J. Am. Chem. Soc. 123 (2001) 12518.
- [10] J.I. Van der Vlugt, T.B. Rauchfuss, S.R. Wilson, Chem. Eur. J. 12 (2006) 90.
- [11] J. Ekström, M. Abrahamsson, C. Olson, J. Bergquist, F.B. Kaynak, L. Eriksson, L. Sun, H.-C. Becker, B. Åkermark, L. Hammarström, S. Ott, Dalton Trans. 38 (2006) 4599.
- [12] X. Zhao, I.P. Georgakaki, M.L. Miller, J.C. Yarbrough, M.Y. Darensbourg, J. Am. Chem. Soc. 123 (2001) 9710.
- [13] J.L. Nehring, D.M. Heinekey, Inorg. Chem. 42 (2003) 4288.
- [14] R. Mejia-Rodriguez, D. Chong, J.H. Reibenspies, M.P. Soriaga, M.Y. Darensbourg, J. Am. Chem. Soc. 126 (2004) 12004.
- [15] R.E. Davis, J. Org. Chem. 23 (1958) 1767.