Luminescent silver nanoparticles stabilised by a crown ether capped with an organometallic cluster

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Abstract

Monolayer-protected clusters of silver have been synthesised by the $NaBH_4$ reduction of a mixture of silver nitrate and the crown ether (6-mercaptohexyloxy)methyl-15-crown-5, or the triosmium cluster derivative $Os_3(\mu\text{-H})(CO)_{10}$[(6-mercaptohexyloxy)methyl-15-crown-5]. The nanoparticles showed good stability, are soluble in a wide range of organic solvents, and are luminescent.
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1. Introduction

Engineered metallic nanoparticles are of great interest because of potential applications in catalysis, nanoscale electronics, and photoluminescent and electroluminescent devices [1]. In particular, monolayer-protected clusters (MPCs) of gold and silver show good stability, tunable solubility and relative ease of characterization; capping reagents for such MPCs have included alkanethiolates, unsaturated carboxylates, amines and isocyanates [2]. A recent interesting example is that of silver nanoparticles fabricated from a two-armed polymer with a crown ether core, *viz.*, [poly(styrene)]-dibenzo-18-crown-6-[poly(styrene)], which exhibited photoluminescence [3]. Furthermore, there have also been applications based on the shift in plasmon frequencies resulting from aggregation of such nanoparticles [4].

We have been interested in the preparation of nanoparticles with the appropriate substrates as molecular model for the study of substrate-surface interactions. Ideally, such a model molecular system should be monodispersed and have suitable spectroscopic handles. Some related examples include metallic nanoparticles functionalized with borane clusters [5], transition metal carbonyls such as $Cr(CO)_4(L)$

and $Re(CO)_3(L)Br$ (L = 2,3-bis(2′-pyridyl)pyrazine) [6], and our recent synthesis of Ag nanoparticles stabilized by the water-soluble organometallic surfactant $[Os_3(\mu\text{-H})(CO)_{10}S(CH_2)_{10}COO]Na$ [7]. We became interested in examining if we may be able to construct photoluminescent silver nanoparticles stabilized with the crown ether (6-mercaptohexyloxy)methyl-15-crown-5 (**4**), as well as with the silver salt of the triosmium cluster derivatized $Os_3(\mu\text{-H})(CO)_{10}$[(6-mercaptohexyloxy)methyl-15-crown-5] (**6**); the latter may provide us with a spectroscopic handle to study the substrate-surface interaction in these nanoparticles.

2. Results and discussion

The route adopted for the synthesis of the crown ether **4** followed those of published procedures [4a,8]. The $NaBH_4$ reduction of silver nitrate in the presence of **4** in a chloroform/water biphasic system led to an immediate colour change to dark brown [9]. The change in color is an indication of the formation of silver nanoparticles (Scheme 1); these silver nanoparticles could be dispersed in a wide range of organic solvents, including chloroform and toluene.

The TEM images showed that the particles are spherical, with diameters of about 5 nm (Fig. 1); this is compara-

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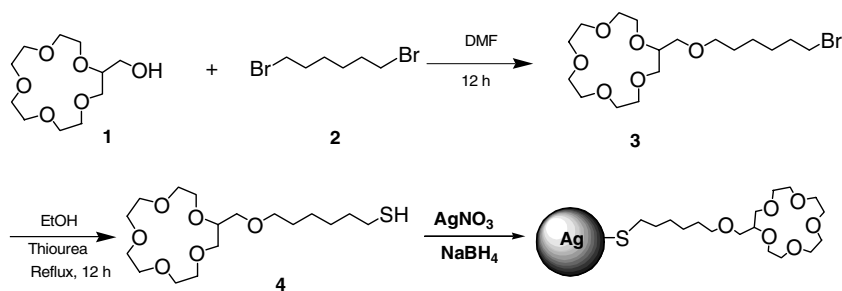
Scheme 1.

ble to silver nanoparticles stabilised by alkanethiols [10]. The association of **4** with the silver nanoparticles was also confirmed by EDX. Refluxing (2 h) a suspension of these particles in methanol solutions of the nitrate of Ag^+, Na^+ or K^+ afforded particles which were soluble in water only, indicating complexation of these ions by the crown ether. The resultant nanoparticles remained spherical, with sizes of about 2 nm for the Ag^+ complex, and about 7 nm for the Na^+ and K^+ complexes.

The UV–Vis spectrum (toluene solution) of the silver nanoparticles capped with **4** displayed a broad and unsymmetrical surface plasmon band at 450 nm (Fig. 2a); this is red shifted compared to unprotected silver particles (390 nm) [7]. In contrast, the surface plasmon band for that complexed with Ag^+ was blue shifted to 411 nm (Fig. 2d). No emission band was observed when a toluene solution of the uncomplexed nanoparticles was excited at 450 nm (Fig. 3a). In contrast, visible luminescence at 488 nm was observed for that complexed with Ag^+ (Fig. 3b); similar emission was also observed for those complexed with Na^+ and K^+. These changes in the emission with the cation suggest that they are associated with aggregation of silver nanoparticles, but these aggregates are presumably fairly dynamic in nature as they do not show up on the TEM images; this is in contrast to that reported for the gold analogues [4a].

The synthetic route to the osmium carbonyl cluster derivatised crown ether $Os_3(\mu\text{-H})(CO)_{10}$[(6-mercaptohexyl-
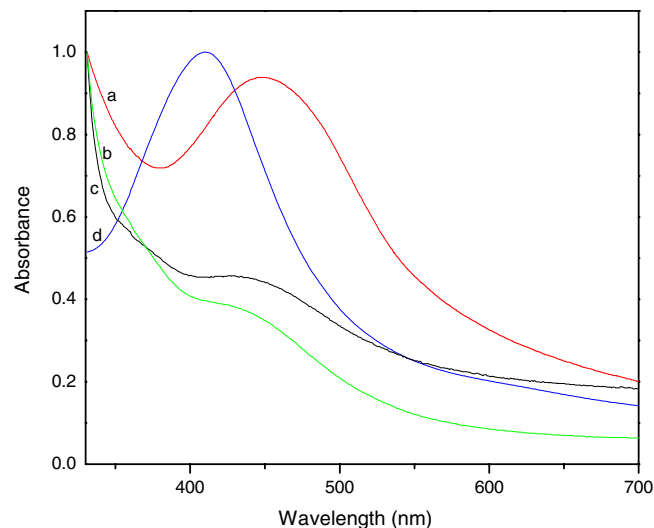

Fig. 2. UV–Vis spectra of silver nanoparticles capped with **4**: (a) in toluene, (b) after reflux with aqueous sodium nitrate, (c) after reflux with aqueous potassium nitrate, and (d) after reflux with aqueous silver nitrate.

oxy)methyl-15-crown-5] (**5**) and its reaction product with silver nitrate, $Os_3(\mu\text{-H})(CO)_{10}$[(6-mercaptohexyloxy)methyl-15-crown-5]-silver nitrate (**6**) is shown in Scheme 2. The structure features of **5** and **6** were identified on the basis of mass spectrometry, and IR and ^1H NMR spectroscopy. Their ^1H NMR spectra showed the expected
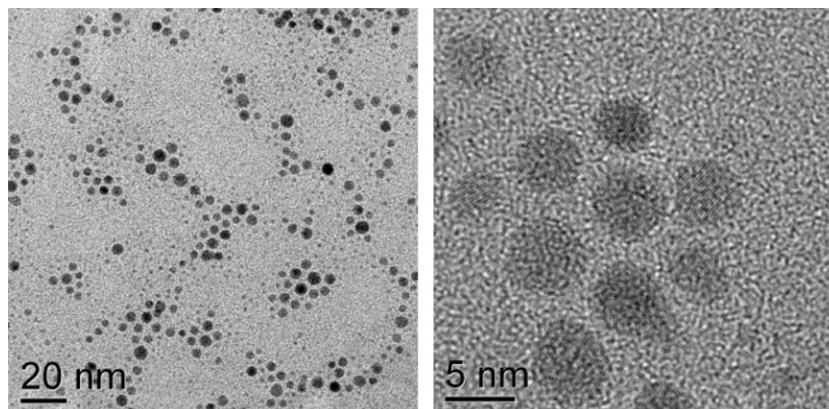

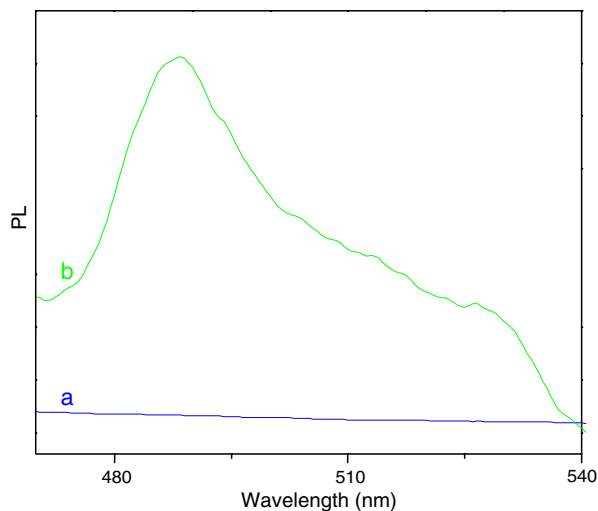Fig. 1. TEM and HR-TEM micrographs of dried silver nanoparticles capped with **4**.

Fig. 3. Emission spectra of silver nanoparticles capped with **4**: (a) in toluene and (b) after reflux with aqueous silver nitrate.

Fig. 4. UV–Vis and emission spectra of silver nanoparticles stabilized by **6**.

resonance at −17.45 ppm, which is characteristic of a μ-H hydride in thiolate-bridged triosmium clusters [11].

The preparation of silver nanoparticles stabilized by **6** followed the procedure for **4** above, i.e., by NaBH₄ reduction of an aqueous silver nitrate solution (2 equivalent) with a chloroform solution containing **6**; a similar attempt at the preparation of gold nanoparticles from NaBH₄ reduction of HAuCl₄ and **6** afforded only insoluble black aggregated materials and unreacted **6**. The resultant silver nanoparticles were spherical, with sizes ranging from 5 to 12 nm, and exhibited a surface plasmon band (410 nm, toluene solution) as well as strong fluorescence (484 nm) on excitation at 410 nm (Fig. 4); these properties are similar to those reported for the silver nanoparticles stabilized with a two-armed polymer with a crown ether core [3], and the water-soluble tiopronin monolayer-protected silver clusters [12], reported earlier. In contrast, silver nanoparticles prepared by photolysis of AgNO₃ with **5** in toluene afforded small nanoparticles (∼2 nm) which showed no fluorescence.

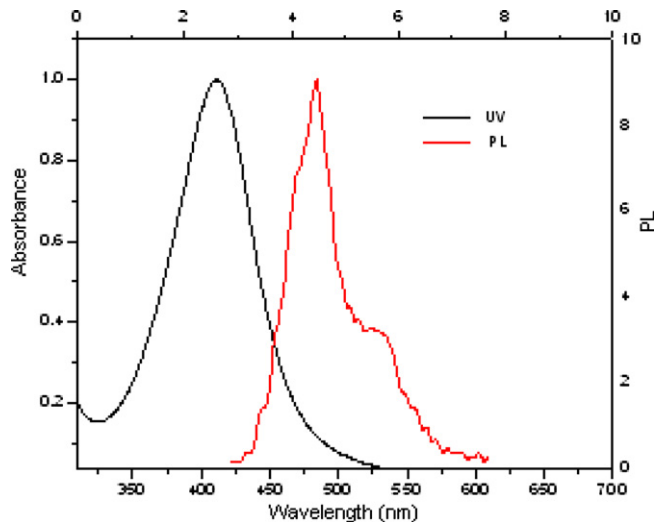While the IR spectrum of the nanoparticles obtained from **6** showed broad peaks for the carbonyl signals com-

pared with the free osmium salt **6**, the ¹H NMR spectrum (in CDCl₃) exhibited no hydride signal. Similarly, for the nanoparticles prepared by photolysis with **5**, there were also significant shifts in the carbonyl stretches. These suggest that there may be significant interaction between the osmium cluster core and the silver nanoparticles. Molecular compounds containing similar interactions in the form of Os–Ag bonds are known [13]. On the other hand, the observation of an emission spectrum points to the aggregation of silver nanoparticles, probably via the same mechanism as for **4**.

3. Concluding remarks

We have shown that silver nanoparticles protected with the crown ether (6-mercaptohexyloxy)methyl-15-crown-5, or its triosmium cluster derivative Os₃(μ-H)(CO)₁₀[(6-mercaptohexyloxy)methyl-15-crown-5], can be prepared by the usual chemical reduction method. The nanoparticles showed good stability, are soluble in a wide range of organic solvents, and are luminescent.
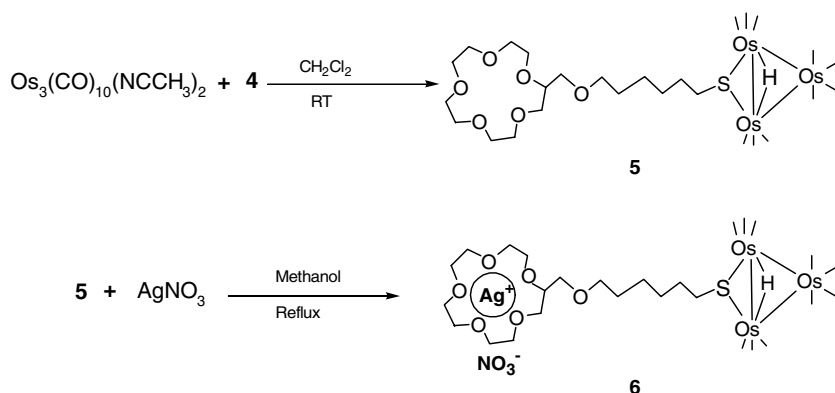
Scheme 2.

4. Experimental

4.1. General procedures

All synthetic steps up to compound **6** were carried out under an atmosphere of argon using standard Schlenk techniques. Photochemical reactions were performed with a Hanovia 450 W UV lamp, with a nominal λ_{max} of 254 nm. ^{1}H NMR spectra were recorded on a Bruker ACF300 NMR spectrometer as CDCl$_3$ solutions unless otherwise stated; chemical shifts reported are referenced against the residual proton signals of the solvents. UV–Vis spectra were recorded using a Shimadzu UV-1601 PC spectrometer. TEM images were recorded on a JEOL JEM 3010 TEM at an accelerating voltage of 300 kV. TEM samples were prepared by placing a drop of the silver colloids onto a carbon-coated Cu grid. All elemental analyses were performed by the microanalytical laboratory at NUS. The cluster Os$_3$(CO)$_{10}$(NCCH$_3$)$_2$ was prepared according to the literature method [14], from Os$_3$(CO)$_{12}$ which was purchased from Oxkem Ltd. and used as supplied. The crown ethers **4** and **5** were synthesized by a modified procedure from the literature as given below [4a,8]. All other reagents were from commercial sources and used without further purification.

4.2. Synthesis of (6-bromohexyloxy)methyl-15-crown-5 (3)

A suspension of 2-(hydroxymethyl)-15-crown-5 (0.41 g, 1.64 mmol) and NaOH (77 mg, 1.93 mmol) in THF was stirred at room temperature. After 30 min, 1,6-dibromo-hexane (1.27 ml, 8.50 mmol) was added, and the mixture was stirred overnight. The reaction was then quenched with methanol, the solvent removed by rotary evaporation, and the residue was taken up in CH$_2$Cl$_2$ (100 ml) and washed several times with water. After drying over Na$_2$SO$_4$, the solvent was evaporated and the residue purified by column chromatography on silica, using a solvent gradient from hexane/EtOAc (1:1, v/v) to EtOAC, to yield a pale yellow oil. Yield: 0.38 g, 56%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.30–1.65 (m, 6H), 1.78–1.93 (m, 2H), 3.3–3.45 (m, 7H) 3.52–3.78 (m, 18H). FAB-MS: m/z 435.3 ([M + Na]$^+$).

4.3. Synthesis of (6-mercaptohexyloxy)methyl-15-crown-5 (4)

To a stirred solution of **3** (400 mg, 0.97 mmol) in ethanol (40 ml) was added thiourea (405 mg, 5.32 mmol). The reaction mixture was heated under reflux for 6 h, and the solvent was then removed under reduced pressure. The resulting solid residue was mixed with KOH (497 mg, 8.72 mmol) and deionized water (40 ml), and then refluxed for 3 h. This was then acidified with 1 M aq. HCl and then extracted with dichloromethane. The organic layer was separated, dried over MgSO$_4$, and the solvent was then distilled off under reduced pressure. The residue was purified by TLC on silica gel plates (hexane/EtOAc, 3:1, v/v, as elu-

ant) to yield **4** as a white solid. Yield = 200 mg (56.4%). ^{1}H NMR: δ 1.22–1.28 (m, 5H, 2CH$_2$ + SH), 1.45–1.54 (m, 4H, 2CH$_2$), 2.32 (q, 2H, CH$_2$S), 3.32–3.38 (m, 4H, CH$_2$O), 3.50–3.60 (m, 19H, crown-CH's). Anal. Calc. for C$_{17}$H$_{34}$O$_6$S: C, 55.71; H, 9.35; S, 8.75. Found: C, 55.45; H, 9.39; S, 9.21%. FAB-MS: m/z 366.51 (M$^+$).

4.4. Synthesis of Os$_3$(μ-H)(CO)$_{10}$[(6-mercaptohexyloxy)-methyl-15-crown-5] (5)

The cluster Os$_3$(CO)$_{10}$(NCCH$_3$)$_2$ (200 mg, 0.21 mmol) was stirred with **4** (48 mg, 0.13 mmol) in dichloromethane (30 ml) at room temperature for 12 h. The solvent was removed under reduced pressure and the product was purified by TLC to yield **5** as a yellow solid. Yield = 140 mg (57.5%). IR (CH$_2$Cl$_2$) ν(CO): 2108 (w), 2066 (s), 2057 (w), 2020 (s), 1996 (m) cm^{-1}; ν(CH): 2922 (m), 2875 (m) cm^{-1}. ^{1}H NMR: δ 1.25–1.47 (m, 4H), 1.50–1.68 (m, 4H), 2.32 (t, 2H, CH$_2$S), 3.35–3.44 (m, 4H), 3.50–3.65 (m, 19H), −17.41 (s, 1H, OsHOs). Anal. Calc. for C$_{27}$H$_{34}$SO$_{16}$-SOs$_3$: C, 26.64; H, 2.82; S, 2.63. Found: C, 27.12; H, 2.90; S, 2.45. FAB-MS: m/z 1218.2 (M$^+$).

4.5. Synthesis of Os$_3$(μ-H)(CO)$_{10}$[(6-mercaptohexyloxy)-methyl-15-crown-5]-silver nitrate (6)

To a sample of **5** (100 mg, 0.08 mmol) in methanol (20 ml) was added silver nitrate (42 mg, 0.25 mmol). The mixture was refluxed for 3 h, cooled to room temperature, and the solvent was removed under reduced pressure to afford **6** as a yellow solid. Yield = 90 mg (88%). IR (CH$_2$Cl$_2$) ν(CO): 2110 (w), 2064 (s), 2021 (s), 1944 (m) cm^{-1}; ν(CH): 2922 (m), 2857 (m) cm^{-1}. ^{1}H NMR: δ 1.32–1.45 (m, 4H), 1.54–1.73 (m, 4H), 2.52 (q, 2H), 3.35–3.46 (m, 4H) 3.50–3.68 (m, 19H), −17.43 (s, 1H). Anal. Calc. for C$_{27}$H$_{34}$AgNO$_{19}$Os$_3$S: C, 23.59; H, 2.07; S, 3.00. Found: C, 24.05; H, 1.91; S, 2.63. FAB-MS: m/z 1386.7 (M$^+$).

4.6. Synthesis of silver nanoparticles protected with 5 by photochemical method

A solution of AgNO$_3$ (20 mg, 0.12 mmol) and **5** (5 mg, 4.1 μmol) in toluene was photolysed for about 5 h. The brown ppt obtained was collected by centrifuge and washed with toluene and water in turn to get rid of excess **5** and AgNO$_3$.

4.7. Synthesis of silver monolayer-protected clusters from 6 in CHCl$_3$/H$_2$O

An aqueous solution of AgNO$_3$ (34 mg, 0.2 mmol in 20 ml water) was mixed with a solution of tetraoctylammonium bromide (109 mg, 0.2 mmol) in chloroform (20 ml). The mixture was stirred for 1 h to ensure complete transfer of the silver into the organic layer. A solution of **6** (62 mg, 0.05 mmol) in chloroform (20 ml) was added dropwise to the vigorously stirred reaction mixture. After stirring for

5 mins, aqueous $NaBH_4$ (5 ml, 0.1 M) was added. With the addition of a few drops of $NaBH_4$, the color changed immediately from yellow to dark brown. The mixture was stirred overnight and the organic phase was separated, washed with distilled water and dried over anhydrous sodium sulphate. The solvent was removed to yield a black solid. The black solid was was dissolved in dichloromethane (ca. 5 ml) and the mixture was diluted with hexane (200 ml) and stored at 0 °C overnight. The functionalized silver nanoparticles were then collected as a brownish black precipitate. The precipitate was exhaustively washed with hexane and re-dispersed in toluene.

Acknowledgement

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.018.

References

[1] (a) L.A. Dick, A.D. McFarland, R.P. Van Duyne, J. Phys. Chem. B 106 (2002) 853;
(b) J. Davies, Nanobiology 3 (1994) 5;
(c) G. Schmid, V. Maihack, F. Lantermann, S. Peschel, J. Chem. Soc. Dalton Trans. (1996) 589;
(d) H. Ohde, C.M. Wai, J. Kim, M. Ohde, J. Am. Chem. Soc. 124 (2002) 4540;
(e) T. Sun, K. Seff, Chem. Rev. 94 (1994) 857.
[2] (a) A.C. Templeton, W.P. Wuelfing, R.W. Murray, Acc. Chem. Res. 33 (2000) 27;
(b) A. Manna, T. Imae, M. Iida, N. Hisamatsu, Langmuir 17 (2001) 6000;
(c) W. Wang, X. Chen, S. Efrima, J. Phys. Chem. B 103 (1999) 7238.
[3] J. Gao, J. Fu, C. Lin, J. Lin, Y. Han, X. Yu, C. Pan, Langmuir 20 (2004) 9775.
[4] (a) See for example, S.-Y. Lin, S.-W. Liu, C.-M. Lin, C.-H. Chen, Anal. Chem. 74 (2002) 330;
(b) J.J. Storhoff, A.A. Lazarides, R.C. Mucic, C.A. Mirkin, R.L. Letsinger, G.C. Schatz, J. Am. Chem. Soc. 122 (2000) 4640;
(c) J.J. Storhoff, R. Elghanian, R.C. Mucic, C.A. Mirkin, R.L. Letsinger, J. Am. Chem. Soc. 120 (1998) 1959;
(d) J. Schmitt, G. Decher, W.J. Dressick, S.L. Brandow, R.E. Geer, R. Shashidar, J.M. Calvert, Adv. Mater. 9 (1997) 61;
(e) C.P. Collier, R.J. Saykally, J.J. Shiang, S.E. Henrichs, J.R. Heath, Science 277 (1997) 1978;
(f) R. Elghanian, J.J. Storhoff, R.C. Mucic, R.L. Letsinger, C.A. Mirkin, Science 277 (1997) 1078.
[5] G. Schmid, R. Pugin, W. Meyer-Zaika, U. Simon, Eur. J. Inorg. Chem. (1999) 2051.
[6] (a) H. Tan, L. Wong, M.Y. Lai, G.S.M. Kiruba, W.K. Leong, M.W. Wong, W.Y. Fan, J. Phys. Chem. B 109 (2005) 19657;
(b) B. Vlckova, P. Matejka, J.W.M. van Outersterp, T.L. Snoeck, D.J. Stufkens, Inorg. Chem. 33 (1994) 2132.
[7] M.O.E. Ahmed, W.K. Leong, J. Organomet. Chem. 691 (2006) 1055.
[8] S. Flink, B.A. Boukamp, A. van den Berg, F.C.J.M. van Veggel, D.N. Reinhoudt, J. Am. Chem. Soc. 120 (1998) 4652.
[9] M. Brust, J. Fink, D. Bethell, D.J. Schiffrin, C.J. Kiely, J. Chem. Soc. Chem. Commun. (1995) 655.
[10] Y.-S. Shon, E. Cutler, Langmuir 20 (2004) 6626.
[11] E.W. Ainscough, A.M. Brodie, R.K. Coll, B.A. Coombridge, J.M. Waters, J. Organomet. Chem. 556 (1998) 197.
[12] T. Huang, R.W. Murray, J. Phys. Chem. B 107 (2003) 7434.
[13] (a) See for example, B.F.G. Johnson, R. Khattar, J. Lewis, P.R. Raithby, J. Chem. Soc. Dalton Trans. (1989) 1421;
(b) S.R. Drake, B.F.G. Johnson, J. Lewis, J. Chem. Soc. Dalton Trans. (1989) 505;
(c) S.R. Drake, B.F.G. Johnson, J. Lewis, J. Organomet. Chem. 340 (1988) C31;
(d) S.B. Colbran, C.M. Hay, B.F.G. Johnson, F.J. Lahoz, J. Lewis, P.R. Raithby, J. Chem. Soc. Chem. Commun. (1986) 1766;
(e) M.I. Bruce, E. Horn, J.G. Matisons, M.R. Snow, J. Organomet. Chem. 286 (1985) 271;
(f) M. Fajardo, M.P. Gomez-Sal, H.D. Holden, B.F.G. Johnson, J. Lewis, R.C.S. McQueen, P.R. Raithby, J. Organomet. Chem. 267 (1984) C25.
[14] J.N. Nicholls, M.D. Vargas, Inorg. Synth. 28 (1989) 234.