Synthesis of monodisperse chromium nanoparticles from the thermolysis of a Fischer carbene complex†

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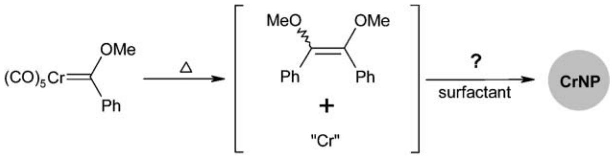
We successfully synthesized monodisperse chromium nanoparticles from the thermolysis of a Fischer carbene complex.

The development of uniform nanometer-sized particles has been a major research focus because of their many technological and fundamental properties.[1] Various nanoparticles of transition metals and their oxides have been synthesized, and their magnetic and catalytic properties characterized. In the synthesis of transition metal nanoparticles, the thermolysis of metal carbonyl compounds, such as $Co_2(CO)_8$,[2] $Fe(CO)_5$,[3] and $W(CO)_6$,[4] have been frequently used. Recently, tailored organometallic precursors were used to synthesize high-quality nanoparticles. For example, the Chaudret group demonstrated the shape-controlled synthesis of ZnO[5] and Co[6] nanoparticles *via* an organometallic chemical approach.

Although chromium and chromium oxide nanoparticles are expected to exhibit interesting magnetic[7] and catalytic[8] properties, there have been very few reports[9] on the synthesis of monodisperse chromium and chromium oxide nanoparticles. Consequently, we attempted to synthesize chromium nanoparticles from the thermal decomposition of $Cr(CO)_6$ in the presence of various surfactants. However, we were not able to synthesize Cr nanoparticles because $Cr(CO)_6$ is thermally stable up to 300 °C and readily sublimes at temperatures >100 °C. Therefore, a chromium–carbene complex was employed as a precursor for the synthesis because it is a thermally labile zero-valent organo-chromium compound.[10]

In the past, the chemistry of the Fischer carbene complexes has been extensively pursued by organic and organometallic chemists.[11] Intensive research interest has been focused on identifying novel organic thermal reactions of Fischer carbene complexes, including radical dimerization,[12] carbene transfer reactions[13] and cyclization.[11] These unique thermal reactions result from the unique activity of the de-ligated carbene mode at high temperatures. In addition, the thermal decomposition behaviour of metal carbene complexes has been a very interesting research topic.[13] In contrast to the previous reports that focused on the organic part of the carbene complexes, this study examined the metal fragment. It was reasoned that the metal fragments could make a good metal source for the synthesis of chromium nanoparticles if a Cr–carbene complex was thermally decomposed in the presence of a suitable surfactant (Scheme 1). This report demonstrates the successful use of a chromium Fischer carbene complex as a precursor for the size-controlled synthesis of Cr nanoparticles. It was found that trioctylphosphine (TOP) is the best surfactant in the current synthesis of Cr nanoparticles.



Scheme 1 Proposed mechanism.

The following describes the typical synthesis of 2.5 nm sized Cr nanoparticles. 0.1 g of chromium Fischer carbene complex, which was synthesized using a method reported elsewhere,[11] was dissolved in 3 mL of TOP. The carbene solution was injected into a 3 mL TOP solution at 300 °C under an argon atmosphere. After the injection, the reaction temperature was reduced to 250 °C. The reaction temperature was slowly increased to 300 °C and the resulting solution was aged at this temperature for 1.5 h. During this process, the colour of the reaction mixture turned black. The reaction mixture was cooled to room temperature and then poured into 30 mL of ethanol, resulting in precipitation. A powder form of the nanoparticles was retrieved by centrifugation, which was

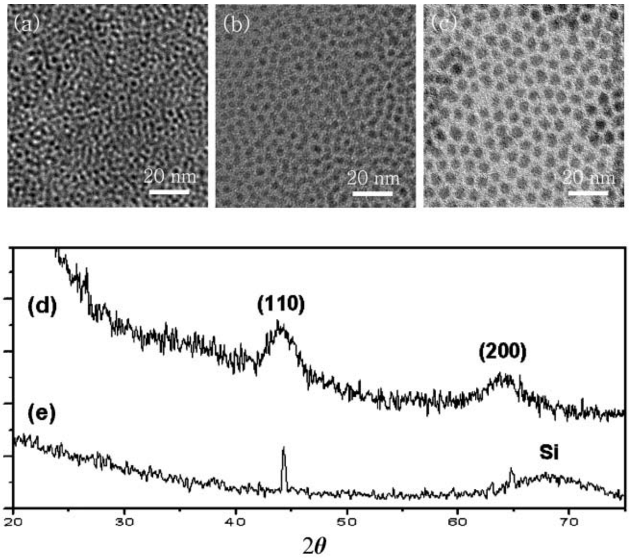


Fig. 1 TEM images of Cr nanoparticles with particles sizes of (a) 2.5 nm, (b) 4.5 nm and (c) 6.0 nm. XRD patterns of 4.5 nm Cr nanoparticles (d) freshly synthesized, and (e) after annealing at 500 °C under argon.

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† Electronic supplementary information (ESI) available: Fig. S1: HRTEM image of and ED pattern of 6.0 nm Cr nanoparticles. See http://www.rsc.org/suppdata/cc/b4/b411656a/

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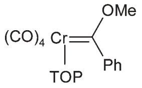
Table 1 Size control experiments

Entry	(TOP/DOE) ml injected	TOP in reaction pot/ml	Size of nanoparticles/nm
1	3/0	3	2.5 (±0.3)
2	4/1	4	4.5 (±0.4)
3	2/3	4	6.0 (±0.4)

redispersed in chloroform. The TEM image shows monodisperse 2.5 nm sized nanoparticles (Fig. 1(a)). The X-ray diffraction (XRD) pattern (Fig. 1(d)) and high-resolution TEM image (see ESI†) shows that the nanoparticles are poorly crystalline. In order to characterize clearly the crystal structure of the nanoparticles, the sample were annealed at 500 °C under an argon atmosphere. The XRD pattern after the annealing clearly showed two peaks at 2θ 44 and 64°, which correspond to (110) and (200) reflections of cubic Cr structure (JCPDS #06-0694, *Im3m* space group. The FT-IR spectrum of the synthesized nanoparticles showed a C–P vibration peak at 1460 cm^{-1}, demonstrating that the nanoparticles were stabilized by TOP. The thermal behaviour of chromium Fischer carbene complexes in TOP solvent was investigated in order to obtain some insight in the nanoparticle formation mechanism. The chromium Fischer carbene complex was readily transformed to compound **1**, which was characterized by ^{1}H, ^{13}C, ^{31}P NMR, IR spectroscopy and elemental analysis.[14]



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It was reasoned that one carbonyl ligand of the chromium Fischer carbene was easily substituted by TOP. This can be contributed to the unique activity of Fischer carbene complexes.[15] It is noteworthy that $Cr(CO)_6$ showed no reactivity to TOP at 300 °C.

Next, an attempt was made to control the size of the chromium nanoparticles. It is well known that the use of two surfactants with a different binding ability is a useful method for controlling the size of nanoparticles.[16] This study screened different types of surfactants and found that dioctyl ether (DOE) is a good surfactant since it was observed to reduce the decomposition rate of the carbene complex. When 0.1 g of the carbene precursor dissolved in 1 mL of dioctyl ether and 4 mL of TOP were injected into 4 mL TOP at 300 °C, 4.5 nm sized Cr nanoparticles were produced (Fig. 1(b) and Table 1). When 0.1 g of the precursor dissolved in 3 mL of dioctyl ether and 2 mL of TOP were injected in 4 mL of TOP at 300 °C, we obtained 6.0 nm sized nanoparticles (Fig. 1(c)). When >3 mL dioctyl ether was employed, nanoparticles were not produced.

The synthesized Cr nanoparticles were highly sensitive to air.[17] They were easily oxidized to form Cr_2O_3 when exposed to air. It is well known that pure chromium metal is easily oxidized to Cr_2O_3, which is known to be the most thermodynamically stable form of chromium oxide. Our attempts to prepare the other controlled chromium oxide species such as CrO_2 are in progress.

In conclusion, we demonstrated the successful use of a chromium Fischer carbene complex as a precursor for the synthesis of monodisperse chromium nanoparticles. Because the carbenes are usually very reactive and do not change the oxidation state of coordinated metals, we expect that these carbene complexes would make good precursors for the synthesis of nanoparticles that cannot be readily prepared using conventional precursors.

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Notes and references

1 (*a*) A. P. Alivisatos, *Science*, 1996, **271**, 933; (*b*) K. J. Klabunde, *Nanoscale Materials in Chemistry*, Wiley-Interscience: New York, 2001; (*c*) T. Hyeon, *Chem. Commun.*, 2003, 927; (*d*) G. Schmid, *Nanoparticles: From Theory to Application*, Wiley-VCH, Weinheim, 2004; (*e*) C. Pacholski, A. Kornowsli and H. Weller, *Angew. Chem., Int. Ed.*, 2002, **41**, 1188; (*f*) A. L. Rogach, D. V. Talapin, E. V. Shevchenko, A. Kornowski, M. Haase and H. Weller, *Adv. Funct. Mater.*, 2002, **12**, 653; (*g*) S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989.

2 (*a*) E. V. Shevchenko, D. V. Talapin, A. L. Rogach, A. Kornowski, M. Haase and H. Weller, *J. Am. Chem. Soc.*, 2002, **124**, 11480; (*b*) E. V. Shevchenko, D. V. Talapin, H. Schnablegger, A. Kornowski, Ö. Festin, P. Svedlindh, M. Haase and H. Weller, *J. Am. Chem. Soc.*, 2003, **125**, 9090.

3 (*a*) V. F. Puntes, K. M. Krishnan and A. P. Alivisatos, *Science*, 2001, **291**, 2115; (*b*) J.-I. Park and J. Cheon, *J. Am. Chem. Soc.*, 2001, **123**, 5743; (*c*) S.-J. Park, S. Kim, S. Lee, Z. G. Khim, K. Char and T. Hyeon, *J. Am. Chem. Soc.*, 2000, **122**, 8581; (*d*) T. Hyeon, S. S. Lee, J. Park, Y. Chung and H. B. Na, *J. Am. Chem. Soc.*, 2001, **123**, 12798.

4 K. Lee, W. S. Seo and J. T. Park, *J. Am. Chem. Soc.*, 2003, **125**, 3408.

5 F. Dumestre, B. Chaudret, C. Amiens, M.-C. Fromen, M.-J. Casanove, P. Renaud and P. Zurcher, *Angew. Chem., Int. Ed.*, 2002, **41**, 4286.

6 M. Monge, M. L. Kahn, A. Maisonnat and B. Chaudret, *Angew. Chem., Int. Ed.*, 2003, **42**, 5321.

7 (*a*) W. Abdul-Razzaq and M. S. Seehra, *Phys. Status Solidi A*, 2002, **193**, 94; (*b*) E. Fawcett, *Rev. Mod. Phys.*, 1988, **60**, 209, and references therein; (*c*) A. W. Overhauser, *Phys. Rev.*, 1962, **128**, 1437; (*d*) H. Zabel, *J. Phys.: Condens. Matter.*, 1999, **11**, 9303; (*e*) A. Gupta, X. W. Li and G. Xiao, *J. Appl. Phys.*, 2000, **87**, 6073; (*f*) J. M. D. Coey and M. Venkatesan, *J. Appl. Phys.*, 2002, **91**, 8345; (*g*) R. K. Zheng, H. Liu, Y. Wang and X. X. Zhang, *Appl. Phys. Lett.*, 2004, **84**, 702.

8 (*a*) S. M. Al-Zahrani, N. O. Elbashir, A. E. Abasaeed and M. Abdulwahed, *Ind. Eng. Chem. Res.*, 2001, **40**, 781; (*b*) N. Ikenaga, T. Tsuruda, K. Senma, T. Yamaguchi, Y. Sakurai and T. Suzuki, *Ind. Eng. Chem. Res.*, 2000, **39**, 1228; (*c*) L. R. Mentasty, O. F. Gorriz and L. E. Cadús, *Ind. Eng. Chem. Res.*, 2001, **40**, 136; (*d*) M. P. McDaniel, *Adv. Catal.*, 1982, **33**, 47; (*e*) J. P. Hogan, D. D. Norwood and C. A. Ayres, *J. Appl. Polym. Sci.*, 1981, **36**, 49.

9 (*a*) M. Green and P. O'Brien, *Chem. Commun.*, 2001, 1912; (*b*) R. D. Tilley and D. A. Jefferson, *J. Mater. Chem.*, 2002, **12**, 3809.

10 It has been reported that some palladium complexes having carbene mode were decomposed to form the metallic nanoparticles under thermal conditions: (*a*) D. S. McGuinness, J. Melinda, K. J. Cavell, B. W. Skelton and A. H. White, *Organometallics*, 1999, **18**, 1596; (*b*) R. R. Deshmukh, R. Rajagopal and K. V. Srinivasan, *Chem. Commun.*,

2001, 1544; (*c*) L. Xu, W. Chen and J. Xiao, *Organometallics*, 2000, **19**, 1123; (*d*) V. Caló, A. Nacci, A. Monopoli, S. Laera and N. Cioffi, *J. Org. Chem.*, 2003, **68**, 2929.

11 (*a*) K. H. Dötz, E. O. Fischer, P. Hofmann, F. R. Kreissel, U. Schubert and K. Weiss, *Transition Metal Carbene Complexes*, Verlag Chemie, Deerfield Beach, FL, 1983; (*b*) K. H. Dötz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 587; (*c*) C. P. Casey, in *Transition Metal Organometallics in Organic Synthesis*, ed. H. Alper, Academic: New York, 1976, ch. 3; (*d*) W. D. Wulff, in *Advances in Metal-Organic Chemistry*, ed. L. S. Liebeskind, JAI, Greenwich, 1987, vol. **1**.; (*e*) J. Barluenga, J. Santamaria and M. Tomas, *Chem. Rev.*, 2004, **104**, 2259; (*f*) M. A. Sierra, *Chem. Rev.*, 2000, **100**, 3591.

12 J. Barluenga, F. Rodríguez and F. J. Fañanás, *Chem. Eur. J.*, 2000, **6**, 1930.

13 C. P. Casey and R. L. Anderson, *J. Chem. Soc., Chem. Commun.*, 1975, 895.

14 To a one-neck flask were added trioctyl phosphine (2 mL), and the chromium Fischer carbene complex (0.2 g). The solution was heated at 70 °C. The color of solution turned from red to yellow. The product was isolated by flash chromatography (eluent hexane–ether = 1:4) 65% isolated yield. Characterization data: ^{1}H NMR ($CDCl_3$, 500 MHz): 7.31 (d, J = 7.4 Hz, 2H), 7.25 (t, J = 7.2 Hz, 2H), 7.15 (t, J = 7.1 Hz, 1H), 3.35 (s, 3H), 2.14 (m, 6H), 1.34–1.24 (m, 36H), 0.87 (t, J = 7.0 Hz, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): 14.0, 16.8, 17.3, 21.7, 22.5, 28.7, 28.8, 30.7, 30.9, 31.6, 123.1, 127.0, 129.0, 130.3, 131.1, 157.4, 222.5, 228.0, 301.8 ppm; ^{31}P NMR ($CDCl_3$, 202 MHz) 34.4 ppm. Anal. Calc. for $C_{36}H_{59}O_5P_1Cr_1$: C, 66.03; H, 9.08. Found: C, 66.46; H, 8.78%. IR (neat) ν_{CO} 1957, 1897 cm^{-1}.

15 Although clear experimental evidence was not obtained, it is believed from previous reports on the thermal reactions of the Fischer carbene complex that the carbene transfer reactions appeared to begin at a high reaction temperature.

16 S.-W. Kim, J. Park, Y. Jang, Y. Chung, S. Hwang and T. Hyeon, *Nano Lett.*, 2003, **3**, 1289.

17 **CAUTION**! Sometimes the well washed nanoparticles will combust in air!.