

Use of ionic liquids (ILs) for the IL-anion size-dependent formation of Cr, Mo and W nanoparticles from metal carbonyl $M(\text{CO})_6$ precursors†

Engelbert Redel,^a Ralf Thomann^b and Christoph Janiak^{*a}

Received (in Cambridge, UK) 22nd November 2007, Accepted 3rd March 2008

First published as an Advance Article on the web 14th March 2008

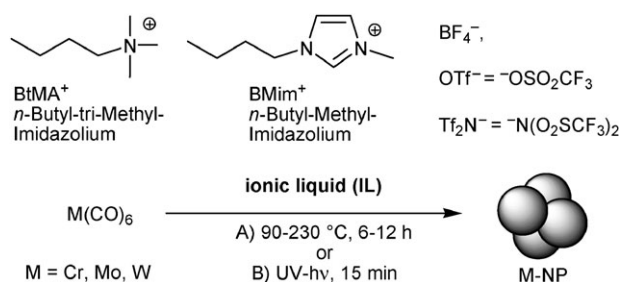
DOI: 10.1039/b718055a

Stable chromium, molybdenum and tungsten nanoparticles are obtained reproducibly by thermal or photolytic decomposition under argon from mononuclear metal carbonyl precursors $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) suspended in the ionic liquids $\text{BMim}^+\text{BF}_4^-$, $\text{BMim}^+\text{OTf}^-$ and $\text{BtMA}^+\text{Tf}_2\text{N}^-$ ($\text{BMim}^+ = n$ -butyl-methyl-imidazolium, $\text{BtMA}^+ = n$ -butyl-trimethyl-ammonium, $\text{Tf}_2\text{N}^- = \text{N}(\text{O}_2\text{SCF}_3)_2$, $\text{OTf}^- = \text{O}_3\text{SCF}_3$) with a very small and uniform size of 1 to 1.5 nm in $\text{BMim}^+\text{BF}_4^-$ which increases with the molecular volume of the ionic liquid anion to ~100 nm in $\text{BtMA}^+\text{Tf}_2\text{N}^-$ [characterization by transmission electron microscopy (TEM), dynamic light scattering and transmission electron diffraction (TED) analysis].

Syntheses and applications of transition-metal nanoparticles are of contemporary interest in several areas of science.¹ In particular, W and Mo nanoparticles can be used for olefin metathesis reactions.² The synthesis of defined and stable metal nanoparticles (MNPs) is of high importance.³

Metal nanoparticles can be stabilized by the ionic charge, high polarity, high dielectric constant and supramolecular network⁴ of ionic liquids (ILs). According to the DLVO (Derjaguin–Landau–Verwey–Overbeek) theory⁵ ILs provide an electrostatic protection in the form of a “protective shell” for MNPs, so that no extra stabilizing molecules are needed.⁶ Most known metal nanoparticle syntheses in ILs are carried out through the reduction of metal salts by hydrogen gas,^{7–9} photochemical¹⁰ or electroreduction/electrodeposition.¹¹ Recently, Fe_2O_3 nanoparticles were synthesized by thermal decomposition of $\text{Fe}(\text{CO})_5$ + stabilizers in $\text{BMim}^+\text{Tf}_2\text{N}^-$.¹² Here we report the preparation of Cr, Mo and W MNPs by thermal or photochemical decomposition under argon of the mononuclear metal carbonyls $M(\text{CO})_6$ in ILs (Scheme 1).^{†13}

Green Cr, brown Mo or gray-blue W nanoparticle dispersions (ESI† Fig. S25–S27) are obtained through decomposition from their metal carbonyl in ionic liquids. The dispersions are found to be stable for six months and longer under argon atmosphere. Also, extremely small MNPs of Cr, Mo and W in



Scheme 1 Formation of Cr, Mo and W nanoparticles by thermal or photolytic decomposition of metal carbonyls under argon in ionic liquids.

the range of about 1 to 1.5 nm with a narrow, albeit not monodisperse, size distribution could be reproducibly synthesized in $\text{BMim}^+\text{BF}_4^-$ (Fig. 1 and Fig. 2, Table 1). Nanoparticles of this small size are novel. Nanoparticles obtained in $\text{BtMA}^+\text{Tf}_2\text{N}^-$ are larger, ranging from about 70 to 150 nm (Table 1). Such large nanoparticles can easily be separated, *e.g.* by simple centrifugation (10 min at 2000 rpm under argon) from the IL. TED (transmission electron diffraction) studies show that the larger Cr, Mo and W NPs produced under argon are crystalline (Fig. 3, ESI† Fig. S14, S18, S23), with the diffraction patterns corresponding to the metal lattices, thereby proving their metallic character and the absence of significant oxidation.

Furthermore, we synthesized the M-oxide nanoparticles (Fig. 4) for comparison to the Cr, Mo and W NPs. For the M-oxides the $M(\text{CO})_6/\text{IL}$ mixture was subjected to the same decomposition conditions, albeit under air.† The M-oxide NPs have different colors from the MNP suspensions (ESI† Fig.

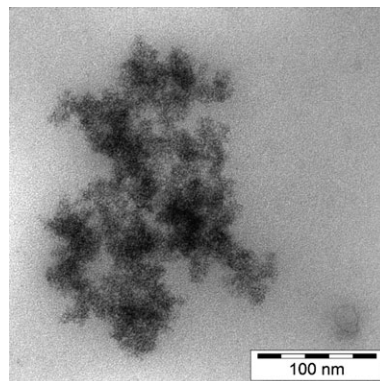


Fig. 1 TEM of W NPs from $\text{W}(\text{CO})_6$ in $\text{BMim}^+\text{BF}_4^-$ by thermal decomposition (entry 1 in Table 1). See footnote *e* in Table 1.

^a Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, D-79104 Freiburg, Germany. E-mail: janiak@uni-freiburg.de; Fax: +49 761 2036147; Tel: +49 761 2036127

^b FMF (Freiburger Material Forschungszentrum), Universität Freiburg, Stefan-Meier-Str. 21, D-79104 Freiburg, Germany. E-mail: ralf.thomann@fmf.uni-freiburg.de; Tel: +49 761 2035379

† Electronic supplementary information (ESI) available: Materials and instrumentation, synthesis, statistical graphs for dynamic light scattering, additional TEM and TED pictures, photographs of dispersions. See DOI: 10.1039/b718055a

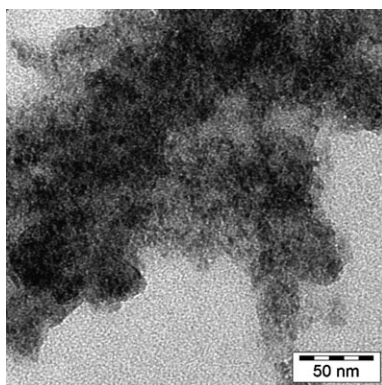


Fig. 2 TEM of Mo NPs from $\text{Mo}(\text{CO})_6$ in $\text{BMim}^+\text{BF}_4^-$ by photolytic decomposition (entry 7 in Table 1). See footnote *e* in Table 1.

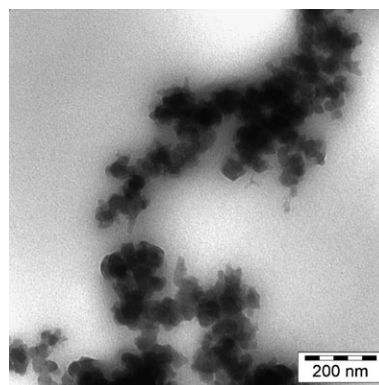


Fig. 4 TEM of Cr-oxide NPs from $\text{Cr}(\text{CO})_6$ in $\text{BtMA}^+\text{Tf}_2\text{N}^-$ by thermal decomposition (entry 12 in Table 1).

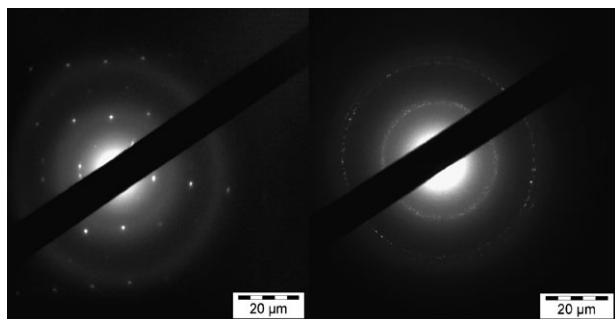


Fig. 3 TED patterns of a single W NP (left) and an ensemble of W NPs (right) from $\text{W}(\text{CO})_6$ in $\text{BtMA}^+\text{Tf}_2\text{N}^-$ by thermal decomposition under Ar (entry 4 in Table 1). The black bar is the beam stopper. The *d*-values match with the *d*-spacing of W metal.¹⁴

S23–25), have a broader size distribution (Table 1) and show no crystallinity (ESI† Fig. S15 and S24).

A comparison of Mo NPs produced under thermal and photolytic decomposition shows only slight differences in median size and size distribution (Table 1). Nanoparticles produced by photolysis give somewhat larger particles because of a faster decomposition process in the ionic liquid.

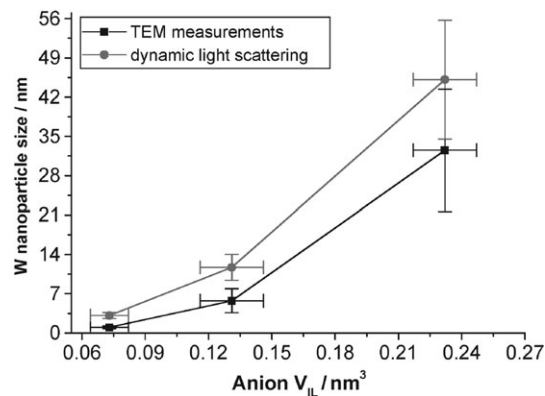


Fig. 5 Correlation between the molecular volume of the ionic liquid anion (V_{IL}) and the observed W nanoparticle size with standard deviations as error bars (from TEM and dynamic light scattering, ESI† Fig. S1–S11).

A correlation exists between the molecular volume of the anion in the ionic liquid and the synthesized metal nanoparticles, shown here for, but not limited to, tungsten. The size of the Cr, Mo and W nanoparticles increases with the molecular volume of the IL anion (Table 1, Fig. 5). MNPs (core) are

Table 1 MNP and M-oxide NP (M = Cr, Mo and W) size and size distribution in different ionic liquids

	Ionic liquid ^a	$V_{\text{IL-anion}}/\text{nm}^3$ ¹⁸ (standard deviation σ)	Metal carbonyl	TEM NP median diameter/nm, (standard deviation σ) ^b	Dynamic light scattering NP median diameter/nm, (standard deviation σ) ^c
1	$\text{BMim}^+\text{BF}_4^-$	0.073 (± 0.009)	$\text{W}(\text{CO})_6$	≤ 1.5 (± 0.3) ^e	3.1 (± 0.5)
2	$\text{BMim}^+\text{OTf}^-$	0.131 (± 0.015)	$\text{W}(\text{CO})_6$	5.7 (± 2.1)	11.7 (± 2.3)
3	$\text{BMim}^+\text{Tf}_2\text{N}^-$	0.232 (± 0.015)	$\text{W}(\text{CO})_6$	33 (± 11)	45 (± 11)
4	$\text{BtMA}^+\text{Tf}_2\text{N}^-$	0.232 (± 0.015)	$\text{W}(\text{CO})_6$	67 (± 32)	97 (± 33)
5	$\text{BtMA}^+\text{Tf}_2\text{N}^-$	0.232 (± 0.015)	$\text{W}(\text{CO})_6/\text{air}$	91 (± 83)	163 (± 47)
6	$\text{BMim}^+\text{BF}_4^-$	0.073 (± 0.009)	$\text{Mo}(\text{CO})_6$	≤ 1.5 (± 0.3) ^e	2.5 (± 0.6)
7	$\text{BMim}^+\text{BF}_4^-$	0.073 (± 0.009)	$\text{Mo}(\text{CO})_6^d$	$\sim 1.0\text{--}2.0$ (± 0.6) ^e	3.8 (± 1.1)
8	$\text{BtMA}^+\text{Tf}_2\text{N}^-$	0.232 (± 0.015)	$\text{Mo}(\text{CO})_6$	150 (± 30)	258 (± 89)
9	$\text{BtMA}^+\text{Tf}_2\text{N}^-$	0.232 (± 0.015)	$\text{Mo}(\text{CO})_6/\text{air}$	— (layers, ESI S19)	— (layers)
10	$\text{BMim}^+\text{BF}_4^-$	0.073 (± 0.009)	$\text{Cr}(\text{CO})_6$	≤ 1.5 (± 0.3) ^e	3.0 (± 0.6)
11	$\text{BtMA}^+\text{Tf}_2\text{N}^-$	0.232 (± 0.015)	$\text{Cr}(\text{CO})_6$	—	51 (± 12)
12	$\text{BtMA}^+\text{Tf}_2\text{N}^-$	0.232 (± 0.015)	$\text{Cr}(\text{CO})_6/\text{air}$	33 (± 10)	62 (± 16)

^a See Scheme 1. ^b From TEM measurements, statistical evaluation of the total sample pictures. ^c Hydrodynamic radius, median diameter from the first 3 measurements at 633 nm in *n*-butyl-imidazole (see ESI Fig. S1–S11). ^d Photolytic decomposition for 15 min at 200 to 450 nm. ^e The TEM pictures with particles of average median diameters of less than 1.5 nm show electron dense cloudy structures. Due to scattering caused by the surrounding ionic liquid resolution of the TEM is limited and particles below 1.5 nm are hardly resolved.

considered stabilized in the ILs by the formation of “protective” anionic and cationic layers (shells) around them in a “core-shell system”.^{6,15} We suggest that the thickness of the stabilizing shells around an MNP depends on the IL molecular ion volumes. According to DLVO theory⁵ the first inner shell must be anionic, then the IL anion will have the greatest influence on the size and electrostatic stabilization of the Cr, Mo and W nanoparticle.

The anion molecular volume determines the region of the nanoparticle size. IL parameters like density, viscosity, conductivity and surface tension also correlate with the volume of the anion in the ionic liquid and could influence nanoparticle nucleation and growth,¹⁶ although the supramolecular imidazolium-anion clusters of the IL should be taken into account.⁴ The IL cation can be used as a fine-tuning tool in nanosynthesis.⁹ “Pure” imidazolium based ILs should be considered as three-dimensional networks of anions and cations, linked by weak interactions (such as hydrogen bonds, van der Waals and Coulomb forces). ILs should be regarded as supramolecular polymeric structures with a high degree of self-organisation and weak interactions. When mixed with other molecules or MNPs, ILs become nanostructured materials with polar and nonpolar regions.^{4,17,18}

We describe here a simple and reproducibly method for the synthesis and size tailoring of Cr, Mo and W metal nanoparticles with median diameters between ~1–100 nm and narrow size distribution in ionic liquids. The synthesis uses easily commercially available M(CO)₆ metal carbonyls and ILs and can readily be expanded to the broad range of other metal carbonyl complexes. Metal carbonyls are attractive starting materials for nanosyntheses, available in high purity or easily purifiable, e.g. by sublimation.¹⁹

We thank Dr T. Schubert from IoLiTec for donation of ILs.

Notes and references

- V. I. Pârvulescu and C. Hardacre, *Chem. Rev.*, 2007, **107**, 2665.
- P. Braunstein and J. Rosé, in *Metal Clusters in Chemistry*, ed. P. Braunstein, L. A. Oro and P. R. Raithby, Wiley-VCH, Weinheim, 2001, vol. 2, ch. 2, pp. 616–677.
- A. H. Lu, E. L. Salabas and F. Schüth, *Angew. Chem., Int. Ed.*, 2007, **46**, 1222; Y. Mastai and A. Gedanken, in *Chemistry of Nanomaterials*, ed. C. N. R. Rao, A. Müller and A. K. Cheetham, Wiley-VCH, Weinheim, 2004, vol. 1, pp. 113ff; A. Gedanken, *Ultrason. Sonochem.*, 2004, **11**, 47; D. Mahajan, E. T. Papish and K. Pandya, *Ultrason. Sonochem.*, 2004, **11**, 385; J. Park, J. Joo, S. G. Kwon, Y. Jang and T. Hyeon, *Angew. Chem., Int. Ed.*, 2007, **46**, 4630.
- J. Dupont, *J. Braz. Chem. Soc.*, 2004, **15**, 341; C. S. Consorti, P. A. Z. Suarez, R. F. de Souza, R. A. Burrow, D. H. Farrar, A. J. Lough, W. Loh, L. H. M. da Silva and J. Dupont, *J. Phys. Chem. B*, 2005, **109**, 4341; J. Dupont, P. A. Z. Suarez, R. F. de Souza, R. A. Burrow and J. P. Kintzinger, *Chem.–Eur. J.*, 2000, **6**, 2377.
- E. J. W. Verwey and J. T. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Dover Publications, Mineola, New York, 2nd edn, 1999; B. W. Ninham, *Adv. Colloid Interface Sci.*, 1999, **83**, 1.
- G. Schmidt, *Nanoparticles*, Wiley-VCH, Weinheim, 2004, pp. 185–238; M. Antonietti, D. Kuang, B. Smarly and Y. Zhou, *Angew. Chem., Int. Ed.*, 2004, **116**, 5096; D. Astruc, F. Lu and J. R. Aranzaes, *Angew. Chem., Int. Ed.*, 2005, **117**, 8062; H. Kaper, F. Endres, I. Djerdj, M. Antonietti, B. M. Smarsly, J. Maier and Y.-S. Hu, *Small*, 2007, **3**, 1753.
- G. S. Fonseca, G. Machado, S. R. Teixeira, G. H. Fecher, J. Morais, M. C. M. Alves and J. Dupont, *J. Colloid Interface Sci.*, 2006, **301**, 193; G. S. Fonseca, J. B. Domingos, F. Nome and J. Dupont, *J. Mol. Catal. A: Chem.*, 2006, **248**, 10; G. S. Fonseca, A. P. Fonseca, S. R. Teixeira and J. Dupont, *Chem.–Eur. J.*, 2003, **9**, 3263; J. Dupont, G. S. Fonseca, A. F. Umpierre, P. F. P. Fichtner and S. R. Teixeira, *J. Am. Chem. Soc.*, 2002, **124**, 4228.
- T. Gutel, J. Garcia-Antón, K. Pelzer, K. Philippot, C. C. Santini, Y. Chauvin, B. Chaudret and J.-M. Basset, *J. Mater. Chem.*, 2007, **17**, 3290; E. T. Silveira, A. P. Umpierre, L. M. Rossi, G. Machado, J. Morais, G. V. Soares, I. J. R. Baumvol, S. R. Teixeira, P. F. P. Fichtner and J. Dupont, *Chem.–Eur. J.*, 2004, **10**, 3734.
- P. Migowski, G. Machado, L. M. Rossi, G. Machado, J. Morais, S. R. Teixeira, M. C. M. Alves, A. Traverse and J. Dupont, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4814.
- J. M. Zhu, Y. H. Shen, A. J. Xie, L. G. Qiu, Q. Zhang and X. Y. Zhang, *J. Phys. Chem. C*, 2007, **111**, 7629; M. A. Firestone, M. L. Dietz, S. Seifert, S. Trasobares, D. J. Miller and N. J. Zaluzec, *Small*, 2005, **1**, 754.
- K. Peppler, M. Polleth, S. Meiss, M. Rohnke and J. Z. Janek, *Phys. Chem. Chem. Phys.*, 2006, **220**, 1507; A. Safavi, N. Maleki, F. Tajabadi and E. Farjami, *Electrochem. Commun.*, 2007, **9**, 1963; K. Kim, C. Lang and P. A. Kohl, *J. Electrochem. Soc.*, 2005, **152**, E9; F. Endres, M. Bukowski, R. Hempelmann and H. Natter, *Angew. Chem., Int. Ed.*, 2003, **42**, 3428; F. Endres, *Phys. Chem. Chem. Phys.*, 2002, **3**, 144; F. Endres, D. MacFarlane and A. Abbott, *Electrodeposition from Ionic Liquids*, Wiley-VCH, Weinheim, 2008.
- Y. Wang, S. Maksimuk, R. Shen and H. Yang, *Green Chem.*, 2007, **9**, 1051.
- The IL BMim⁺BF₄[−] is stable up to 423 °C. The ILs were dried at high vacuum (10^{−3} mbar) for several days, to avoid especially in the case of BMim⁺BF₄[−] the hydrolysis to HF; F. Endres and S. Z. El Abedin, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2101; P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2nd edn, 2007, vol. 1, pp. 32ff and 61; R. P. Swatloski, J. D. Holbrey and R. D. Rogers, *Green Chem.*, 2003, **5**, 361; G. A. Baker and S. N. Baker, *Aust. J. Chem.*, 2005, **58**, 174.
- STOE WinXPow version 1.10, data base, STOE & Cie GmbH, Darmstadt, Germany, 2002.
- A. N. Shipway, E. Katz and I. Willner, *ChemPhysChem*, 2000, **1**, 18; T. Cassagneau and J. H. Fendler, *J. Phys. Chem. B*, 1999, **103**, 1789; C. D. Keating, K. K. Kovaleski and M. J. Natan, *J. Phys. Chem. B*, 1998, **102**, 9404.
- H. Jin, B. O'Hare, J. Dong, S. Arzhantsev, G. A. Baker, J. F. Wishart, A. J. Benesi and M. Maroncelli, *J. Phys. Chem. B*, 2008, **112**, 81; G. Machado, J. D. Jackson, T. da Vargas, S. R. Teixeira, L. H. Ronchi and J. Dupont, *Int. J. Nanotechnol.*, 2007, **4**, 541; C. N. R. Rao, S. R. C. Vivekchand, K. Biswas and A. Govindaraj, *Dalton Trans.*, 2007, 3728; J. M. Slattey, C. Daguene, P. Dyson, T. J. S. Schubert and I. Krossing, *Angew. Chem., Int. Ed.*, 2007, **46**, 5384; P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772.
- T. J. Gannon, G. Law, R. P. Watson, A. J. Carmichael and K. R. Seddon, *Langmuir*, 1999, **15**, 8429; G. Law, R. P. Watson, A. J. Carmichael and K. R. Seddon, *Phys. Chem. Chem. Phys.*, 2001, **3**, 2879.
- J. N. C. Lopes, M. F. C. Gomes and A. A. H. Padua, *J. Phys. Chem. B*, 2006, **110**, 16816; J. N. C. Lopes and A. A. H. Padua, *J. Phys. Chem. B*, 2006, **110**, 3330.
- Metalcarbonyls are poisonous due to the possible liberation of CO and, thus, should be handled with care, yet Fe(CO)₅ and Ni(CO)₄ are industrially produced on a multi-ton scale; see D. G. E. Kerfoot, X. Nickel, E. Wildermuth, H. Stark, G. Friedrich, F. L. Ebenhöch, B. Kühborth, J. Silver and R. Rituper, Iron Compounds, in *Ullmann's Encyclopaedia of Industrial Chemistry*, Wiley, 5th edn (online), 2008.