Journal of Organometallic Chemistry, 229 (1982) 179—184
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ORGANOACTINIDE ELECTROCHEMISTRY. A CYCLIC VOLTAMMETRIC AND COULOMETRIC STUDY OF $(C_5Me_5)_2UCl_2$, $[(C_5Me_5)_2UCl_2 \cdot THF]^-Na^+$, $(C_5Me_5)_2UCl \cdot THF$ AND $(C_5Me_5)_2ThCl_2$

RICHARD G. FINKE *, GLEN GAUGHAN and RICHARD VOEGELI
Department of Chemistry, University of Oregon, Eugene, Oregon, 97403 (U.S.A.)

(Received July 23rd, 1981; in revised form October 22nd, 1981)

Summary

$(C_5Me_5)_2UCl_2$ exhibits a one-electron, reversible reduction to $(C_5Me_5)_2UCl_2^-$ without detectable Cl^- loss, $E_{1/2}$ (CH_3CN) = —1.30 V and $E_{1/2}$ (THF) = —1.22 V vs. SCE, which is shown to correspond to the one-electron, reversible oxidation of isolated $[(C_5Me_5)_2UCl_2 \cdot THF]^-Na^+$ and to be distinct from the irreversible oxidation of $(C_5Me_5)_2UCl \cdot THF$ (Ep_a (THF) = —0.71 V, 50 mV/sec scan rate); the related $(C_5Me_5)_2ThCl_2$ is not reduced even out to —2.7 V.

Recent studies of *f*-element, organoactinide complexes have demonstrated enhanced reactivity relative to their *d*-block, organotransition metal analogues [1,2]. For example, we recently reported that $(C_5Me_5)_2U^{III}Cl \cdot THF$ oxidative additions of alkyl halides proceed by an inner-sphere, atom-abstraction mechanism at rates 10^4—10^7 faster than any known, isolable, *d*-block transition metal reagent reacting by this pathway [2b]. Since the rates of inner-sphere electron transfers or atom abstractions generally reflect the reactions' thermodynamic driving force [3], a measurement of the $E_{1/2}$ for the U^{III}/U^{IV} couple was required to understand this enhanced reactivity *. Moreover, the results presented below comprise the first electrochemical study of bis(pentamethylcyclopentadienyl)-actinide complexes.

Electrochemical experiments on these sensitive actinide complexes were performed on m*M* solutions at ca. 30°C inside a Vacuum Atmospheres inert atmosphere (N_2) dry box using a conventional 3-electrode cell equipped with a Luggin capillary, a spherical Pt or planar glassy carbon microelectrode, a AgCl-coated Ag wire quasi-reference electrode with ferrocene as an internal

---

* Our recent mechanistic study [2b] of $(C_5Me_5)_2UCl \cdot THF$ oxidative additions established that THF loss and the resultant coordinative-unsaturation are one essential component of the enhanced reactivity.

0022-328X/82/0000—0000/$02.75

standard [4,5], and with carefully purified and dried n-$Bu_4N^+PF_6^-$ electrolyte and THF or CH_3CN solvent *. Measured half-wave potentials, $E_{1/2} = [Ep_{(cathodic)} + Ep_{(anodic)}]/2$, are reported vs. a saturated calomel electrode (SCE).

Cyclic voltammetry of $(C_5Me_5)_2UCl_2$ at either glassy carbon or Pt electrodes shows a single, one-electron, reversible wave in CH_3CN, Fig. 1, at $E_{1/2} = -1.30$ V vs. SCE (ΔEp = that of ferrocene internal standard, ca. 77 mV, at 20 mV/sec scan rate, $ip_a/ip_c = 0.81$, $ip_c/(\text{scan rate})^{1/2}$ = a constant, $n = 1.0 \pm 0.1$ by coulometry). Consistent with the assignment of this wave to the U^{IV}/U^{III} couple, cyclic voltammetry of $(C_5Me_5)_2UCl_2$ in CH_3CN containing $PhCH_2Cl$ shows a greatly reduced oxidation current, with the oxidation wave disappearing altogether at slow scan rates, as expected for the consumption of electrogenerated U^{III}, $(C_5Me_5)_2UCl_2^{-\cdot}$, by oxidative addition of $PhCH_2Cl$ [2]. In THF, a single reversible wave is observed for $(C_5Me_5)_2UCl_2$ at $E_{1/2} = -1.22$ V vs. SCE. No further reduction, U^{III} to U^{II}, was observed in either THF or CH_3CN up to a negative potential limit of ca. —2.7 V.

The reversibility of the reduction of $(C_5Me_5)_2UCl_2$ even in CH_3CN suggests that the reduction occurs without Cl^- loss, $(C_5Me_5)_2UCl_2 + e^- \rightleftharpoons (C_5Me_5)_2UCl_2^{-\cdot}$. This explanation is supported by rapid scan experiments which show only the one, reversible wave up to scan rates of 200 V/sec at 30°C (Fig. 1, insert) [7a]. Additional evidence for the retention of Cl^- by $(C_5Me_5)_2UCl_2^{-\cdot}$ was obtained from the 20 minute, room temperature Na(Hg) reduction of $(C_5Me_5)_2UCl_2$ in THF inside a dry box, followed by recrystallization from toluene containing a small percentage of THF, decanting the mother liquor, and drying in vacuo. The resultant green, benzene soluble material is formulated as $[(C_5Me_5)_2UCl_2 \cdot THF]^{-\cdot}Na^+$ based on its elemental analysis and other physical data **. The cyclic voltammogram of this material, Fig. 2, is essentially that previously found for the $(C_5Me_5)_2UCl_2/(C_5Me_5)_2UCl_2^{-\cdot}$ couple, and is clearly different from that of $(C_5Me_5)_2UCl \cdot THF$. A green, THF solution of authentic, analytically pure $(C_5Me_5)_2UCl \cdot THF$ (prepared [1f] by $(C_5Me_5)_2UCl(Me) + H_2$) showed

---

* $Bu_4N^+PF_6^-$ was recrystallized from 95% EtOH 4—6 times and dried two days in vacuo at 100°C over P_2O_5. THF was distilled from Na/benzophenone under N_2 and CH_3CN was distilled two times from CaH_2 under N_2. Noticeable decomposition of $(C_5Me_5)_2UCl_2$ was observed in THF and CH_3CN containing 0.2 *M* Bu_4NPF_6 ($t_{1/2} \approx 0.5$ and 1.0 h, respectively), as evidenced by a color change from orange to yellow concomitant with a decrease in the reversible wave and the appearance of an irreversible wave at ca. —1.6 V. Satisfactory and reproducible results for the U^{III} complexes $(C_5Me_5)_2UCl \cdot THF$ and $[(C_5Me_5)_2UCl_2 \cdot THF]^{-\cdot}Na^+$ were obtainable only in THF and only if fresh solutions $\leqslant$ a few minutes old were examined. The use of reduced, $\leqslant$30°C, temperatures was not examined and could prove useful for the less stable solutions. On the basis of high uranium—halogen bond strengths, a sensitivity to the fluorine-containing PF_6^- was considered but was not unequivocally established experimentally. All the organouranium compounds are very sensitive [6] to trace amounts of impurities and the reproducible data presented hererin was obtained only as the result of many experiments.

** Freshly prepared samples show a λ_{max}(benzene) = 740 nm, a cryoscopic m.w. = 770 ± 130 (calcd. 674), δ (benzene-d_6, C_5Me_5) = —4.7 ppm (line width at half-height = 125 Hz) and elemental analysis: Found: C, 41.96; H, 5.54; Na, 3.11; Cl, 9.32; U, 36.1 ± 0.5. Calcd. (for $[(C_5Me_5)_2UCl_2 \cdot THF]^{-\cdot}Na^+$): C, 42.74; H, 5.68; Na, 3.41; Cl, 10.51; U, 35.29%. Repeat analysis on an independent sample, Found: C, 40.59; H. 5.54; Na, 4.47; Cl, 10.82; U, 34.8 ± 0.5.

Although $\leqslant$1% impurities in fresh samples are detectable by ^1H NMR, decomposition even in a good, $\leqslant$1 ppm O_2 dry box is observed to give products exhibiting a ^1H NMR of δ (benzene-d_6) = 2.97 (s), 4.45 (s), 5.78 (s).

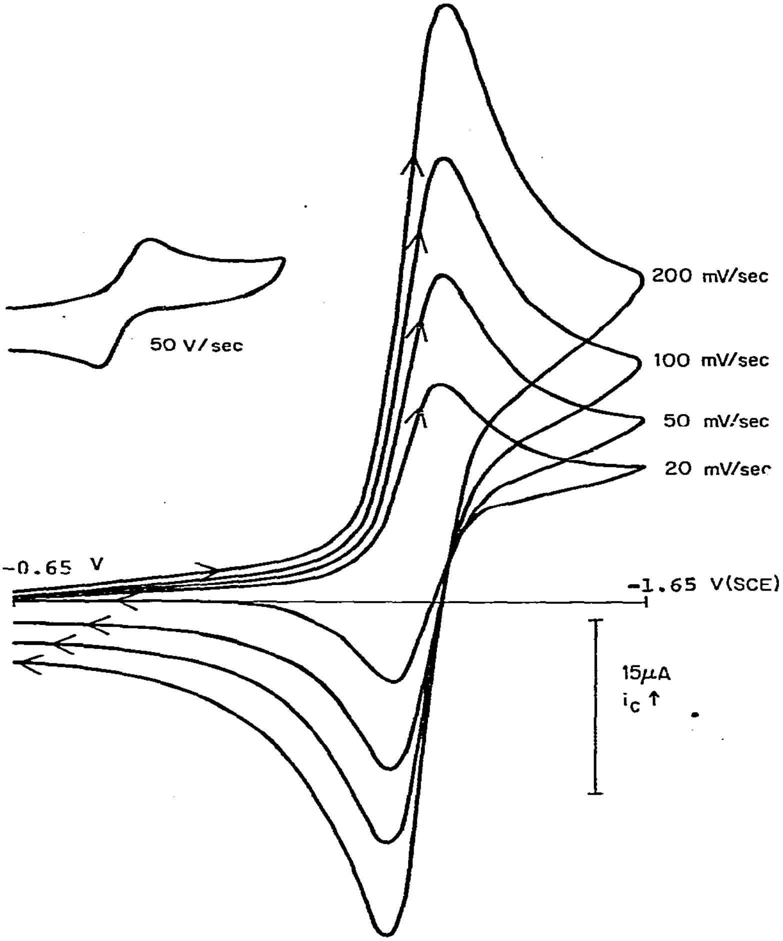

Fig. 1. Cyclic voltammogram at Pt (vs. SCE) of $(C_5Me_5)_2UCl_2$ in CH_3CN containing 0.2 *M* Bu_4NPF_6 and at 20, 50, 100, and 200 mV/sec scan rates. The insert shows an oscilloscope recording of a —0.65 to —1.65 V (SCE) scan at 50 V/sec scan rate but otherwise under the same conditions. The observation of only the $E_{1/2} = -1.30$ V wave ($ip_a/ip_c = 1$) and the lack of a more cathodic wave due to $(C_5Me_5)_2UCl \cdot CH_3CN$ is consistent with Cl^- retention by $(C_5Me_5)_2UCl_2^{\overline{\cdot}}$. Other evidence for $(C_5Me_5)_2UCl_2^{\overline{\cdot}}$ is provided in the text.

an irreversible voltammogram (Fig. 3) with a scan rate-dependent, anodic peak potential $Ep_a = -0.71$ V at 50 mV/sec.

The Cl^- retention by $(C_5Me_5)_2UCl_2^{\overline{\cdot}}$ stands in contrast to the somewhat controversial results [7] for Cp_2TiCl_2 where, at least under certain conditions [7a], rapid Cl^- loss follows the electron transfer in an EC mechanism, $Cp_2TiCl_2 + e^- \rightleftharpoons Cp_2TiCl_2^{\overline{\cdot}}$, then $Cp_2TiCl_2^{\overline{\cdot}}$ + solvent $\rightleftharpoons Cp_2TiCl \cdot$ solvent + Cl^-. The loss of Cl^- from $Cp_2TiCl_2^{\overline{\cdot}}$ but not from $(C_5Me_5)_2UCl_2^{\overline{\cdot}}$ is consistent with the picture of significant ionic bonding [8] and the known Lewis acidity [9] of organoactinides and lanthanides *.

---

* In our hands, a control experiment on ca. 5 m*M* Cp_2TiCl_2 in THF showed an $Ep_a = -0.80$ V (lit. [6] = —0.80 V) and $Ep_a = -0.32$ and —0.56 V in CH_3CN at 100 mV/sec. For $(C_5Me_5)_2UCl_2$, efforts to obtain additional evidence for Cl^- retention by $(C_5Me_5)_2UCl_2^{\overline{\cdot}}$ by checking the dependence of the potentials vs. $[Cl^-]$ [7a] (as added LiCl(THF) or $Bu_4NCl(CH_3CN)$) were unsuccessful since new, complex, and not readily interpretable waves resulted on Cl^- addition.

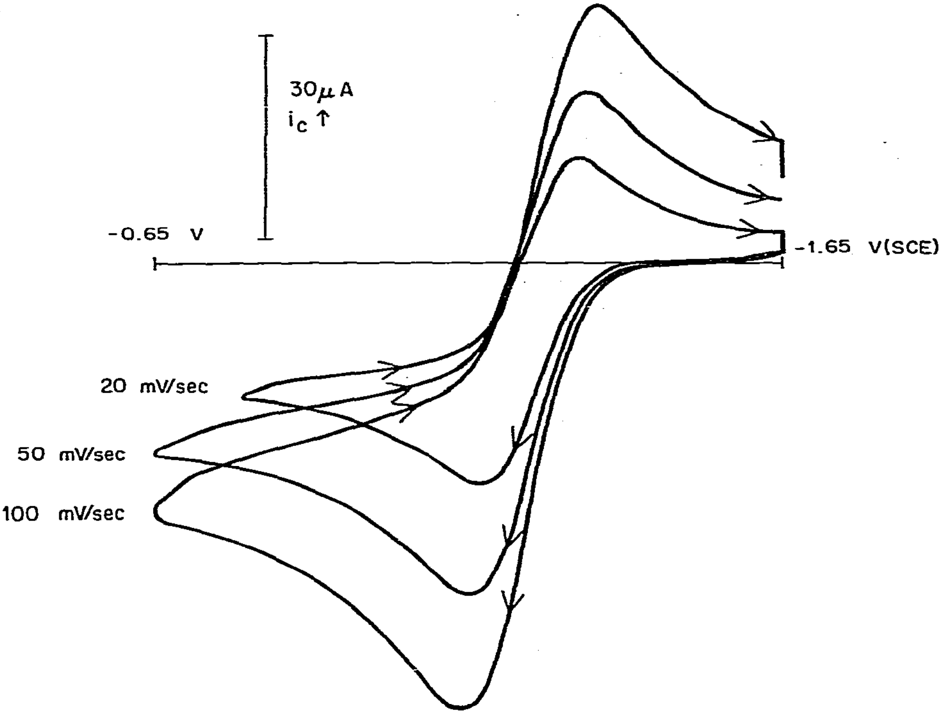

Fig. 2. Cyclic voltammogram at Pt (vs. SCE) of $[(C_5Me_5)_2UCl_2 \cdot THF]^-Na^+$ in THF containing 0.2 *M* Bu_4NPF_6 and at 20, 50, and 100 mV/sec scan rates.

In the case of $(C_5Me_5)_2ThCl_2$, no faradaic current above background was observed in either CH_3CN or THF out to ca. −2.7 V vs. SCE from which a positive limit on the $(C_5Me_5)_2ThCl_2$, Th^{IV}/Th^{III} potential of $E_{1/2} \leqslant -2.7$ V can be estimated assuming, as is likely based on the $(C_5Me_5)_2UCl_2$ results, that there is no large kinetic barrier to the electron transfer. A NMR control showed that $(C_5Me_5)_2ThCl_2$ in THF plus Bu_4NPF_6 did not undergo decomposition.

In summary, $(C_5Me_5)_2UCl_2$ shows a reversible, one-electron reduction without Cl^- loss at −1.22 V in THF while the $E_{1/2}$ for $(C_5Me_5)_2ThCl_2$ lies negative of −2.7 V. When combined with the recent results [7] on Cp_2TiCl_2 and Cp_2ZrCl_2, the following order of increasing difficulty of reduction results ($E_{1/2}$(V) vs. SCE in THF): Cp_2TiCl_2 (apparent $E_{1/2} = -0.80$ V) < $(C_5Me_5)_2UCl_2$ ($E_{1/2} = -1.22$ V) < Cp_2ZrCl_2 (apparent $E_{1/2} = -1.8$ V) ≪ $(C_5Me_5)_2ThCl_2$ ($E_{1/2} \leqslant -2.7$ V). This order demonstrates that while the reversible U^{III}/U^{IV} potential of about −1.2 V provides a reasonably strong driving force to U^{III} oxidative addition reactions [2], the ca. −0.6 V more negative Zr^{III}/Zr^{IV} couple suggests that Zr^{III} [10] oxidative-additions could, depending upon the other factors involved [3], be even more facile than those of U^{III}.

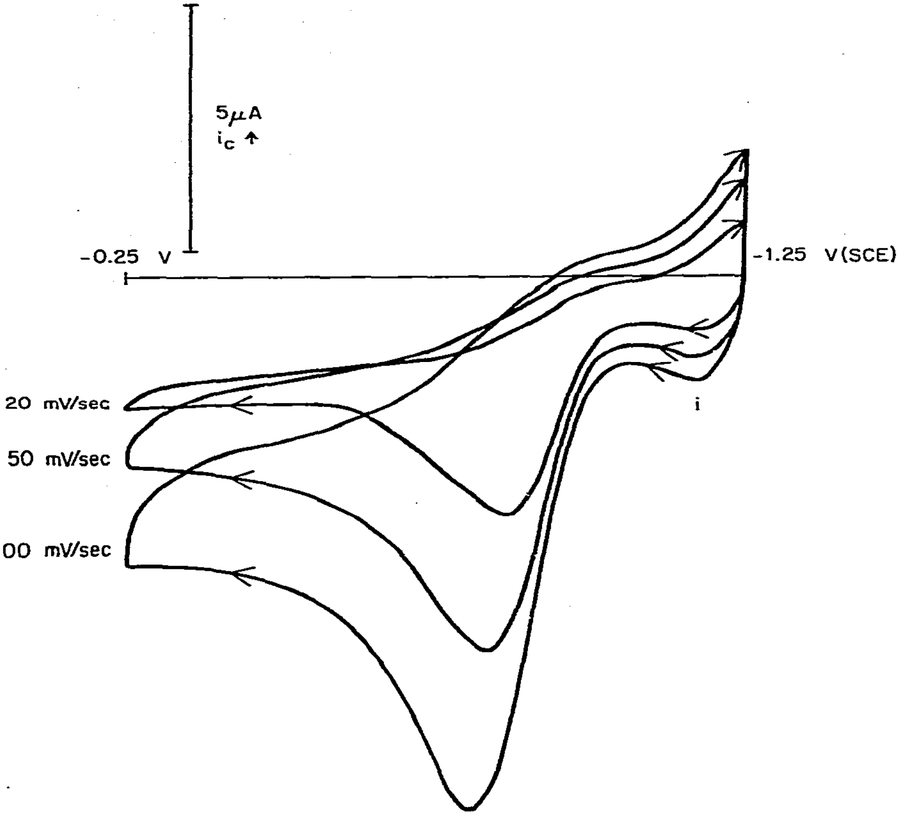

Fig. 3. Cyclic voltammogram at Pt (vs. SCE) of $(C_5Me_5)_2UCl \cdot THF$ in THF containing 0.2 *M* Bu_4NPF_6 and at 20, 50, and 100 mV/sec. A plot of Ep_a vs. log ν gave a line with a slope of 81 mV/decade while, in the same resistive solution, ferrocene showed a linear plot with a 57 mV/decade slope. The small impurity peak labeled "i" was initially absent in solutions of freshly prepared compound but grew in very rapidly.

Acknowledgments

We thank Professor Tobin J. Marks for providing a sample of $(C_5Me_5)_2ThCl_2$ and for the exchange of unpublished information. Financial support was provided by the National Science Foundation. R.G.F. is thankful for a Dreyfus Teacher-Scholar grant (1982—1987).

References

1 (a) J.M. Manriquez, P.J. Fagan, and T.J. Marks, J. Amer. Chem. Soc., 100 (1978) 3939.
(b) J.M. Manriquez, P.J. Fagan, T.J. Marks, C.S. Day and V.W. Day, ibid., 100 (1978) 7112.
(c) P.J. Fagan, J.M. Manriquez and T.J. Marks, in T.J. Marks and R.D. Fischer (Eds.), Organometallics of the *f*-Elements, D. Reidel, Dordrecht, Holland, 1978, p. 113.
(d) T.J. Marks, Prog. Inorg. Chem., 25 (1979) 223.
(e) P.J. Fagan, J.M. Manriquez, T.J. Marks, V.W. Day, S.H. Vollmer, and C.S. Day, J. Amer. Chem. Soc., 102 (1980) 5393.
(f) J.M. Manriquez, P.J. Fagan, T.J. Marks, S.H. Vollmer, C.S. Day and V.W. Day, J. Amer. Chem. Soc., 101 (1979) 5075.
(g) P.J. Fagan, J.M. Manriquez, S.H. Vollmer, C.S. Day, V.W. Day, and T.J. Marks, J. Amer. Chem. Soc., 103 (1981) 2206.

(h) R.G. Bowman, R. Nakamura, P.J. Fagan, R.L. Burwell, Jr. and T.J. Marks, J. Chem. Soc. Chem. Commun., (1981) 257.

(i) E.A. Maatta and T.J. Marks, J. Amer. Chem. Soc., 103 (1981) 3576.

(j) N.M. Edelstein (Ed.), Lanthanide and Actinide Chemistry and Spectroscopy, ACS Symposium Series No. 131, ACS, Washington, D.C., 1980.

2 (a) R.G. Finke, Y. Hirose, G. Gaughan, J. Chem. Soc. Chem. Commun., (1981) 232.

(b) R.G. Finke, D.A. Schiraldi, and Y. Hirose, J. Amer. Chem. Soc., 103 (1981) 1875,

3 (a) R.A. Marcus, J. Phys. Chem., 72 (1968) 891.

(b) A.O. Cohen and R.A. Marcus, ibid., 72 (1968) 4249.

(c) J.F. Endicott, C.L. Wong, J.M. Ciskowski, and K.P. Balakrishnan, J. Amer. Chem. Soc., 102 (1980) 2100.

4 R.R. Gagné, C.A. Koval, G.C. Lisensky, Inorg. Chem., 19 (1980) 2854. The ferrocene vs. SCE potentials measured in our system were comparable to the literature values, $E_{1/2}$ (THF) = 0.51 V [5a] and $E_{1/2}$ (CH_3CN) = +0.41 V [5b].

5 (a) B. Jaun, J. Schwarz, and R. Breslow, J. Amer. Chem. Soc., 102 (1980) 5741.

(b) T. Kuwana, D.E. Bublitz and E. Hoh, ibid., 82 (1960) 5811. These authors report a polarographic $E_{1/4}$ = +0.307 V vs. SCE for 3.25×10^{-3} M ferrocene in 0.2 M $LiClO_4/CH_3CN$ at a Pt foil electrode.

6 J.D.L. Holloway and W.E. Geiger, Jr., J. Amer. Chem. Soc., 101 (1979) 2038. This work (see p. 2039, Cp_2V), our work, and that of others [7b] suggests that the electrochemistry of the most sensitive of the metallocenes and metallocene dihalides are best handled in a vacuum line cell although a good dry box appears to be adequate for most systems. A Hg electrode was not used in the work presented herein since previous studies showed that Cp_2MCl_2 (M = Ti) reacts with Hg, see S.P. Gubin and S.A. Smirnova, J. Organometal. Chem., 20 (1969) 229.

7 (a) Y. Mugnier, C. Moise and E. Laviron, J. Organometal. Chem., 204 (1981) 61.

(b) N. El Murr, A. Chaloyard, and J. Tirouflet, J. Chem. Soc. Chem. Commun., (1980) 446.

(c) Y. Mugnier, C. Moise, and E. Laviron, J. Organometal. Chem., 210 (1981) 69.

(d) N. El Murr, and A. Chaloyard, ibid., 212 (1981) C39.

(e) See also the electrochemical data in: M.F. Lappert, C.J. Pickett, P.I. Riley, and P.I.W. Yarrow, J. Chem. Soc. Dalton, (1981) 805.

8 (a) K.N. Raymond, C.W. Eigenbrot, Jr., Accts. Chem. Res., 13 (1980) 276.

(b) J.P. Clark and J.C. Green, J. Chem. Soc. Dalton, (1977) 505.

(c) N. Rösch and A. Streitwieser, Jr., J. Organometal. Chem., 145 (1978) 195.

(d) J.C. Green, M.R. Kelly, J.A. Long, B. Kanellakopulos, and P.I.W. Yarrow, J. Organometal. Chem., 212 (1981) 329.

9 (a) M.F. Lappert, A. Singh, J.L. Atwood and W.E. Hunter, J. Chem. Soc., Chem. Commun., (1981) 1911; (b) P.L. Watson, J.F. Whitney and R.L. Harlow, Inorg. Chem., 20 (1981) 3271; (c) T.D. Tilley and R.A. Anderson, ibid., 20 (1981) 3267.

10 G.M. Williams, K.I. Gell, and J. Schwartz, J. Amer. Chem. Soc., 102 (1980) 3660, 7619.