Journal of Organometallic Chemistry, 205 (1981) 319—327
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ATTEMPTS TO PREPARE ALKYLIDENE ZIRCONIUM COMPLEXES BY α-HYDROGEN ATOM ABSTRACTION

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(Received July 29th, 1980)

Summary

We prepared several new neopentyl halide complexes of zirconium in order to test whether they could be induced to lose neopentane and give neopentylidene complexes by adding phosphorus or nitrogen donor ligands. $ZrNp_2X_2$ (X = Cl or Br) can be prepared in ether and isolated as a dietherate (an oil). It reacts with L (L = PMe_3, PMe_2Ph, NEt_3, 1/2 DMPE, 1/2 TMEDA) to give $ZrNp_2X_2L_2$. $ZrNp_3Cl$ can be prepared by adding $MgNp_2$ to $ZrNp_2Cl_2(ether)_2$ and isolated by sublimation in 25% yield. On adding PMe_3 or TMEDA, it disproportionates to $ZrNp_4$ and $ZrNp_2Cl_2L_2$. $ZrCp''NpCl_2$ ($Cp'' = \eta^5$-C_5Me_5), $ZrCp''Np_2Cl$, and $ZrCp''Np_3$ were prepared by adding $MgNp_2$ to $ZrCp''Cl_3$. Only the last is a solid, only the first forms an adduct, $ZrCp''NpCl_2(PMe_3)$. None of the complexes decomposed to tractable products in the presence of L. Photolysis of $ZrNp_2Cl_2(PMe_3)_2$ yielded $[Zr(PMe_3)_2Cl_3]_2$ by an apparently complex reaction initiated by homolytic Zr—Np bond fission.

Introduction

The formation of neopentylidene and benzylidene complexes of Nb and Ta by loss of neopentane or toluene (respectively) from an alkyl-niobium(V) or -tantalum(V) complex containing at least two alkyl groups has been known for several years [1]. With the exception of the reaction of DMPE with $W(CCMe_3)(CH_2CMe_3)_3$ to give $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(DMPE)$ [2], this type of reaction has not been observed outside of Group V metals. Therefore, we set out to determine whether it might be found for complexes of Group IV metals. We chose zirconium over titanium since we found titanium(IV) to be

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reduced too easily to titanium(III) [3]. We decided to "induce" α-abstraction by adding phosphorus or nitrogen donor ligands to alkyl halide complexes since this type of reaction yielded a large class of octahedral neopentylidene-niobium and -tantalum complexes and an analogous benzylidene complex [4]. A plausible complex, *mer,trans*-$Zr(CHR)L_3Cl_2$, would be closely related.

Results

$ZrNp_2X_2L_2$ * *complexes*

Zirconium tetrachloride or tetrabromide reacts with two equivalents of $LiCH_2CMe_3$ in ether at 25°C to give lithium chloride and, after removing the ether, a yellow-red oil. An ^1H NMR spectrum of the oil shows one ether molecule per neopentyl ligand, even after many hours in vacuo. We assume there are actually two of each present since the ether can be displaced by phosphorus or nitrogen donor ligands (L) to give crystalline, orange to yellow adducts with the formula $ZrNp_2X_2L_2$ (eq. 1).

$$ZrCl_4 \xrightarrow[\text{ether}]{2LiNp} ZrNp_2X_2(\text{ether})_2 \xrightarrow{2L} ZrNp_2X_2L_2 \qquad (1)$$

(X = Cl, L = PMe_3, PMe_2Ph, NEt_3, $\frac{1}{2}$DMPE, $\frac{1}{2}$TMEDA; X = Br, L = PMe_3, or $\frac{1}{2}$TMEDA)

The ^1H and ^{31}P NMR spectra of the phosphine adducts suggest that these ligands exchange rapidly on the NMR time scale at 25°C. For example, after adding PMe_3 to a sample of $ZrNp_2Cl_2(PMe_3)_2$, the spectrum shows only a single PMe_3 resonance, even at −60°C. In the ^1H NMR spectrum we could also never see coupling of the neopentyl α-protons to phosphorus, presumably for the same reason. Triethylamine, TMEDA, and DMPE bond more strongly to zirconium(IV) than the monodentate phosphines since they will displace them. Free triethylamine and TMEDA also exchange rapidly with coordinated triethylamine and TMEDA, respectively, at 25°C according to ^1H NMR studies. Under these circumstances we cannot tell what the structure of the adducts is for certain but we might expect the bulky neopentyl groups to be *trans* to each other.

The $ZrNp_2X_2L_2$ complexes are not very stable thermally. They decompose at varying rates in bezene at 25—50°C to give about two equivalents of neopentane, a trace of 2,2,5,5-tetramethylhexane, and a black, insoluble tar. Some qualitative data are listed in Table 1. These decomposition reactions are identical if done under 40 psi of ethylene; no 4,4-dimethyl-1-butene, a typical product of the reaction between neopentylidene-niobium or -tantalum complexes and ethylene [1], nor any other plausible organic product (e.g., the metathesis product, 3,3-dimethyl-1-butene), was found by GLC. In CD_2Cl_2 $ZrNp_2Cl_2(TMEDA)$ decomposes cleanly to give one equivalent of neopentane and $ZrNpCl_3(TMEDA)$ (eq. 2). This result suggests that neopentyl radicals and

$$ZrNp_2Cl_2(TMEDA) \xrightarrow[50^\circ C, 12h]{CD_2Cl_2} ZrNpCl_3(TMEDA) + CMe_4(80\%\ d^0, 20\%\ d^1) \qquad (2)$$

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* $Np = CH_2CMe_3$

TABLE 1

APPROXIMATE $t_{1/2}$ FOR THE DECOMPOSITION OF $ZrNp_2X_2L_2$ IN BENZENE [a]

Compound	Time	Conditions
$ZrNp_2Cl_2(PMe_3)_2$	20 h	50°C
$ZrNp_2Cl_2(PMe_3)_2$	5 min	photolysis [b]
$ZrNp_2Br_2(PMe_3)_2$	5 h	50°C
$ZrNp_2Br_2(PMe_3)_2$	30 min	photolysis
$ZrNp_2Cl_2(PMe_2Ph)_2$	20 h	70°C
$ZrNp_2Cl_2(NEt_3)_2$	30 min	25°C
$ZrNp_2Cl_2(DMPE)$	15 h	50°C
$ZrNp_2Cl_2(DMPE)$	5 min	photolysis
$ZrNp_2Cl_2(TMEDA)$	40 h	50°C
$ZrNp_2Br_2(TMEDA)$	30 h	50°C
$Zr(Nph)_2Cl_2(TMEDA)$ [c]	10 h	25°C

[a] The time elapsed when $[ZrNp_2X_2L_2] \approx [CMe_4]$ by ^1H NMR. [b] 550 W Hanovia medium pressure mercury lamp. [c] $Nph = CH_2CMe_2Ph$.

"$ZrNpCl_2(TMEDA)$" are the initial products but does not alone exclude formation of neopentane and a neopentylidene-zirconium complex by α-hydrogen abstraction.

$ZrNp_3ClL$ complexes

One of the possible problems in any α-abstraction reaction where only two alkyl groups are present is that they may never be in the necessary * mutually *cis* relationship long enough for one to abstract an α-hydrogen atom from another. One tactic which avoids this problem is to attempt α-abstraction in trialkyl complexes.

$ZrNp_3Cl$ can be prepared in 25% sublimed yield by reacting $ZrNp_2Cl_2(ether)_2$ with 0.5 equivalents of $MgNp_2$ (eq. 3). It could not be separated from a

$$ZrNp_2Cl_2(ether)_2 + 0.5\ MgNp_2 \xrightarrow[2.\text{sublime}]{1.-78^\circ C,\text{ether}} ZrNp_3Cl \qquad (3)$$

small amount of $ZrNp_4$ [6a,6b] impurity and so was characterized only by ^1H NMR (the chemical shift of the methylene protons is between that in $ZrNp_2Cl_2(ether)_2$ and that in $ZrNp_4$) and by its reactions with donor ligands. Adding one equivalent of PMe_3 to $ZrNp_3Cl$ yields $ZrNp_3Cl(PMe_3)$, but it cleanly disproportionates to $ZrNp_4$ and $ZrNp_2Cl_2(PMe_3)_2$ in 15 minutes at 50°C (eq. 4). The

$$ZrNp_3Cl + PMe_3 \xrightarrow{\text{pentane}} ZrNp_3Cl(PMe_3) \xrightarrow[\text{benzene}]{15\text{min},50^\circ C} 0.5\ ZrNp_4 + 0.5\ ZrNp_2Cl_2(PMe_3)_2 \qquad (4)$$

TMEDA adduct cannot be observed at 25°C, only the disproportionation products (eq. 5). This behavior may be the reason why all attempts to add a

$$ZrNp_3Cl + TMEDA \xrightarrow{\text{pentane}} 0.5\ ZrNp_4 + 0.5\ ZrNp_2Cl_2(TMEDA) + 0.5\ TMEDA \qquad (5)$$

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* In one tantalum system, all evidence suggests that the two neopentyl groups must be *cis* for a successful α-abstraction reaction[5]. *trans*-Dineopentyl complexes are comparatively stable thermally.

third neopentyl group to $ZrNp_2X_2L_2$ yielded only $ZrNp_4$. Evidently, $ZrNp_4$ forms no strong adducts with phosphines or amines so that α-abstraction is not likely in this case either.

η^5-C_5Me_5(Cp") complexes

In an attempt to reduce the likelihood of disproportionation reactions, we switched to the monocyclopentadienyl-neopentyl complexes, a type in which α-abstraction was successful when the metal was tantalum [5].

ZrCp"Cl_3 can be prepared in high yield by treating LiC_5Me_5 with $ZrCl_4$ in ether. It crystallizes as a yellow dietherate from ether but can be obtained white and ether-free by dissolution in toluene followed by removal of all volatiles in vacuo. ZrCp"Cl_3 can be alkylated by $MgNp_2$ to yield ZrCp"$NpCl_2$, ZrCp"Np_2Cl, and ZrCp"Np_3, only the last of which is a solid. A PMe_3 adduct of the first can be isolated but neither ZrCp"Np_2Cl nor ZrCp"Np_3 yields a stable adduct. These complexes are more stable in the presence of PMe_3 than the $ZrNp_2X_2L_2$ species but when they decompose at ~100° C in benzene only insoluble tars are formed.

Neophyl and benzyl complexes

We attempted a few experiments with neophyl and benzyl complexes in order to test whether more bulk in the alkyl group (neophyl) or greater accessibility of the metal center to the donor ligand (benzyl) might help create a situation conducive to α-abstraction.

$Zr(CH_2CMe_2Ph)_2Cl_2$(TMEDA), $Zr(CH_2Ph)_2Cl_2$(TMEDA) and $Zr(CH_2Ph)_2Cl_2(PMe_3)_2$ can be prepared straightforwardly from the dialkyl dietherates, $ZrR_2Cl_2(ether)_2$ *. $Zr(CH_2CMe_2Ph)_2Cl_2$(TMEDA) is less stable thermally than $ZrNp_2Cl_2$(TMEDA) and decomposes in benzene to give two equivalents of t-butylbenzene. Both dibenzyl complexes are very stable thermally. They decomposed little in 12 h at 120° C in toluene.

Photolysis of $ZrNp_2Cl_2(PMe_3)_2$

Many of the alkyl complexes and adducts which we have mentioned so far are sensitive to light. Some qualitative data are shown in Table 1. Since we have observed that α-hydrogen abstraction reactions are accelerated by light [5,7] we decided to investigate one Zr system more closely.

When a benzene solution of $ZrNp_2Cl_2(PMe_3)_2$ is photolyzed for 10 h with a 550 watt Hanovia lamp, insoluble, forest-green crystals form on the container's walls and about 1.6 equivalents of neopentane and about 0.4 equivalents of 2,2,5,5-tetramethylhexane are found in the reaction volatiles by GLC. The green compound is very sensitive to air and turns yellow rapidly at 35° C in any solvent in which it dissolves (CH_2Cl_2, $CHCl_3$, CH_3CN, THF, and C_6H_5Cl). However, since it does not react rapidly with dichloromethane at −20° C, we could obtain an ^1H NMR spectrum. We saw only a doublet for PMe_3. It analyzes as $ZrCl_3(PMe_3)_2$. We postulate that this species has two bridging chloride ligands and a Zr—Zr bond.

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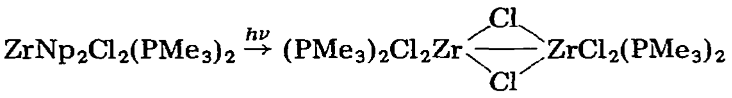
[*] Zucchini et al. [6c], prepared ether-free $Zr(CH_2Ph)_2Cl_2$ from $Zr(CH_2Ph)_4$ and two equivalents of HCl.



$$\mathrm{ZrNp_2Cl_2(PMe_3)_2 \xrightarrow{h\nu} (PMe_3)_2Cl_2Zr\overset{Cl}{\underset{Cl}{\longrightarrow}}ZrCl_2(PMe_3)_2} \qquad (6)$$

(We have prepared more soluble analogs directly from $ZrCl_4L_2$ by reduction with Na amalgam which will be described fully elsewhere (L = triethylphosphine or tributylphosphine) [8]). The reaction is clearly complex, and like photoaccelerated reactions of alkyltantalum compounds [5,7], produces substantial quantities of 2,2,5,5-tetramethylhexane, presumably by coupling of neopentyl radicals. In spite of the reaction's complexity, we observe about 80% of the maximum theoretical yield (66%). These limited results suggest that we will not be able to prepare a neopentylidene complex of zirconium photochemically any more cleanly or selectively than we could neopentylidene [5] or benzylidene [7] complexes of tantalum.

Discussion

None of the alkyls we have prepared here have been reported previously. Their preparation is straightforward if ether is used as the solvent. Hydrocarbon solvents yield $ZrNp_4$, probably since more soluble $ZrNp_xCl_{4-x}$ is alkylated before relatively insoluble $ZrCl_4$. We did not try Grignard reagents but we did try alkylations with $ZnNp_2$: $ZrCl_4$ does not react readily with $ZnNp_2$ in either pentane or ether.

The preparation of alkylidenezirconium complexes by α-abstraction reactions does not appear promising. We cannot entirely exclude formation of a neopentylidene complex in some cases, but if any is formed it is too unstable to survive the reaction conditions. Some of the best evidence against formation of a neopentylidene complex is that the course of one reaction was not altered by adding ethylene. One would expect it to react rapidly with olefins as does a "Lewis acid protected" methylenetitanium complex [9]. The exact mode of decomposition in the absence of light is not certain; the result of decomposition in CD_2Cl_2 to give neopentane-d_1 is open to several interpretations. Photolysis appears to generate neopentyl radicals, a result which is not surprising in view of the results for tantalum [5,7], or the known tendency for d^0 alkyl metals to lose an alkyl radical when irradiated [10].

Why then is α-abstraction in d^0 alkylzirconium complexes apparently unfavorable? Our view now is that a successful α-abstraction reaction in a d^0 alkyl complex requires a special set of conditions. α-Abstraction may be related to homolytic cleavage of the metal—carbon bond, i.e., it can be viewed as abstraction of a "properly activated" α-hydrogen atom by an incipient neopentyl radical generated when L adds to the metal. We believe an α-hydrogen atom is "activated" when the metal attracts electron density from an alkyl α-CH bond, much as has been observed (almost certainly more markedly) in alkylidenetantalum complexes [11]. A crowded coordination sphere and seven-coordinate phosphine complexes also may be important (cf. the octahedral tantalum complexes [4]) so the fact that the donor ligands are lost so readily from Zr could be a significant problem. In short, perhaps we should not be surprised that such a special combination of circumstances is rare.

Can alkylidenezirconium complexes be made another way? We believe they can. One reasonable approach is to transfer an alkylidene ligand from a phosphorane to zirconium(II), a method which was successful in preparing Ta(η^5-C_5H_5)$_2$(CHR)(CH_3) (R = H, Me, Ph) [12]. Schwartz has recently reported that Zr(η^5-C_5H_5)$_2$(CH_2)($PMePh_2$) can be observed in situ spectroscopically by treating Zr(η^5-C_5H_5)$_2$($PMePh_2$)$_2$ with $Ph_3P{=}CH_2$ [13] so that this method, in principle, appears promising.

Experimental

All experiments were performed under prepurified nitrogen in a Vacuum Atmospheres HE-43 dry box using solvents which had been rigorously dried under nitrogen by standard techniques.

Preparation of $ZrNp_2X_2(ether)_2$

$ZrCl_4$ (2.33 g, 10 mmol) was suspended in 60 ml ether. LiNp [14] (1.56 g, 20 mmol) dissolved in 30 ml ether was added dropwise over 1 h to the $ZrCl_4$ at room temperature with stirring. The reaction is photosensitive and should be shielded from light. The yellow-red reaction mixture was stirred for 15 min. The mixture was filtered, and the solvent removed in vacuo to yield a red oil. This oil was extracted into a 60% pentane/40% ether solvent mixture, and again filtered to remove additional LiCl. This solution was used in subsequent preparations of adducts (assuming a quantitative yield). Removing all the solvent in vacuo yielded an oil. $ZrNp_2Br_2(ether)_2$ was prepared analogously.

^{1}H NMR $ZrNp_2Cl_2(ether)_2$ (δ, C_6D_6): 3.31 (q, 4, O($CH_2$$CH_3$)$_2$), 2.37 (s, 2, CH_2CMe_3), 1.28 (s, 9, CMe_3), 1.01 (t, 6, O(CH_2CH_3)$_2$). ^{1}H NMR $ZrNp_2Br_2(ether)_2$ (δ, C_6D_6): 3.31 (q, 4, O(CH_2CH_3)$_2$), 2.43 (s, 2, CH_2CMe_3), 1.30 (s, 9, CMe_3), 1.01 (t, 6, O(CH_2CH_3)$_2$).

Preparation of $ZrNp_2X_2L_2$

PMe_3 (1.52 g, 20 mmol) was added via cold syringe to the pentane/ether solution of $ZrNp_2Cl_2(ether)_2$ prepared above. Yellow crystals of $ZrNp_2Cl_2(PMe_3)_2$ formed in the solution and were collected by filtration. A second crop was obtained by standing the filtrate at −30°C for 5 h. The total yield was 4.10 g (90%). $ZrNp_2Cl_2(PMe_3)_2$ recrystallizes best from ether/pentane solvent mixtures. $ZrNp_2Cl_2$(DMPE), $ZrNp_2Cl_2(PMe_2Ph)_2$, $ZrNp_2Cl_2(NEt_3)_2$, $ZrNp_2Cl_2$(TMEDA), $ZrNp_2Br_2(PMe_3)_2$, and $ZrNp_2Br_2$(TMEDA) were prepared in an analogous manner. The yields varied from 65 to 90%.

Anal. Found for $ZrNp_2Cl_2(PMe_3)_2$: C, 41.87; H, 8.65. $ZrC_{16}H_{40}P_2Cl_2$ calcd.: C, 42.09; H, 8.93%. Anal. Found for $ZrNp_2Cl_2$(TMEDA): C, 45.78; H, 9.20. $ZrC_{16}H_{38}N_2Cl_2$ calcd.: C, 45.69; H, 9.11%. ^{1}H NMR of $ZrNp_2Cl_2(PMe_3)_2$ (δ, C_6D_6): 2.01 (s, 2, CH_2CMe_3), 1.17 (s, 9, CMe_3), 0.83 (d, 9, ^2J(HP) 4 Hz, PMe_3). ^{1}H NMR of $ZrNp_2Cl_2$(DMPE) (δ, C_6D_6): 1.93 (s, 2, CH_2CMe_3), 1.33 (s, 9, CMe_3), 1.23 (m, PCH_2CH_2P), 0.97 (t, 6, ^2J(HP) 3 Hz, PMe_2). ^{1}H NMR $ZrNp_2Cl_2(PMe_2Ph)_2$ (δ, C_6D_6): 7.03—7.49 (complex, 5, Ph), 2.06 (s, 2, CH_2CMe_3), 1.19 (d, 6, ^2J(PH) 3 Hz, PMe_2) 1.07 (s, 9, CMe_3). ^{1}H NMR $ZrNp_2Cl_2(NEt_3)_2$ (δ, C_6D_6): 2.32 (q, 6, N(CH_2CH_3)$_3$), 1.75 (s, 2, CH_2CMe_3), 1.27 (s, 9, CMe_3), 0.83 (t, 9, N(CH_2CH_3)$_3$. ^{1}H NMR $ZrNp_2Cl_2$(TMEDA) (δ, C_6D_6): 2.20 (s, 6,

NCH_3), 1.88 (s, 2, NCH_2), 1.83 (s, 2, CH_2CMe_3), 1.32 (s, 9, CMe_3). ^1H NMR $ZrNp_2Br_2(PMe_3)_2$ (δ, C_6D_6): 2.17 (s, 2, CH_2CMe_3), 1.20 (s, 9, CMe_3), 0.98 (br s, 9, PMe_3). ^1H NMR $ZrNp_2Br_2$(TMEDA) (δ, C_6D_6): 2.17 (s, 6, NCH_3), 2.00 (s, 2, NCH_2), 1.75 (s, 2, CH_2CMe_3), 1.23 (s, 9, CMe_3). ^{13}C NMR $ZrNp_2Cl_2(PMe_3)_2$ (δ, C_6D_6, gated ^1H decoupled): 101.4 (t, J(CH) 106 Hz, CH_2CMe_3), 36.5 (s, CH_2CMe_3), 34.2 (q, J(CH) 125 Hz, CH_2CMe_3), 14.2 (qd, J(CH) 129 Hz, J(CP) 7.8 Hz, PMe_3). ^{13}C NMR $ZrNp_2Cl_2$(TMEDA) (δ, C_6D_6, gated ^1H decoupled): 103.3 (t, J(CH) 105 Hz, CH_2CMe_3), 58.1 (t, J(CH) 130 Hz, NCH_2), 50.6 (q, J(CH) 136 Hz, NCH_3), 36.8 (s, CH_2CMe_3), 34.3 (q, J(CH) 119 Hz, CH_2CMe_3). $^{31}P\{^1H\}$ NMR $ZrNp_2Cl_2(PMe_3)_2$ (δ, C_6D_6): −43.5 (s).

Preparation of $ZrNp_3Cl$

$MgNp_2$ (0.72 g, 4.3 mmol) [15] dissolved in 25 ml of ether was added dropwise to a stirred ether solution of $ZrNp_2Cl_2(ether)_2$ (8.6 mmol in 60 ml ether) at −78° C. The reaction mixture was stirred for 2 h and the ether then removed in vacuo. The resulting brown, oily residue was sublimed for 10 h at 60° C (0.001 mmHg) to yield 0.70 g (25%) yellow crystalline $ZrNp_3Cl$ containing a small amount of $ZrNp_4$.

^1H NMR (δ, C_6D_6): 1.50 (s, 2, CH_2CMe_3), 1.07 (s, 9, CMe_3).

Preparation of $ZrNp_3Cl(PMe_3)$

PMe_3 (0.23 g, 3.0 mmol) was added slowly by syringe to $ZrNp_3Cl$ (0.5 g, 1.5 mmol) dissolved in 10 ml of pentane. The solution remained a pale yellow. The pentane was removed in vacuo to give pale-yellow crystalline $ZrNp_3Cl(PMe_3)$, quantitatively.

^1H NMR (δ, C_6D_6): 1.23 (s, CMe_3), 0.77 (d, ^2J(HP) 4 Hz, PMe_3). The methylene protons must be obscured at this field strength.

Preparation of $ZrCp''Cl_3$

$ZrCl_4$ (1.0 g, 4.3 mmol) and LiCp″ (0.61 g, 4.3 mmol) [16] were stirred together in 60 ml ether for 5 h. The LiCl was filtered off from the yellow solution. The filtrate was concentrated in vacuo to yield several crops of $ZrCp''Cl_3(ether)_x$. This product was extracted into toluene, and the toluene removed in vacuo to yield 1.25 g (85%) ether-free, white $ZrCp''Cl_3$. Anal.: Found: Cl, 31.99. $ZrC_{10}H_{15}Cl_3$ calcd.: Cl, 31.96%. ^1H NMR (δ, C_6D_6): 2.09 (s).

Preparation of $ZrCp''NpCl_2(PMe_3)$

PMe_3 (0.91 g, 12 mmol) was added by syringe to $ZrCp''Cl_3$ (4.0 g, 12 mmol) dissolved in 30 ml ether. $MgNp_2$ (1.0 g, 6.0 mmol), dissolved in 20 ml of ether was added dropwise to this stirred solution over 1 h at room temperature. The reaction mixture was stirred for 2 days during which time the color changed from yellow to orange. The mixture was filtered and the ether was removed in vacuo from the orange filtrate. The resulting oil was extracted into a minimal amount of pentane, which was then cooled to −30° C. Two crops of pale orange crystals were collected. The total yield was 3.45 g (65%).

Anal. Found: C, 48.69; H, 8.01. $ZrC_{18}H_{35}PCl_2$ calcd.: C, 48.63; H, 7.94%. ^1H NMR (δ, C_6D_6): 1.87 (s, 15, C_5Me_5), 1.39 (s, 9, CMe_3), 1.03 (s, 2, CH_2CMe_3), 0.92 (d, 9, ^2J(HP) 5 Hz, PMe_3). ^{13}C NMR (δ, C_6D_6, gated ^1H decoupled): 123.5

(s, C_5Me$_5$), 88.0 (t, J(CH) 110 Hz, CH$_2$CMe$_3$), 35.2 (s, CH$_2$$CMe_3$), 34.4 (q, J(CH) 123 Hz, CMe$_3$), 13.0 (q, J(CH) 127 Hz, J(CP) 13 Hz, PMe$_3$), 12.4 (q, J(CH) 127 Hz, C$_5$$Me_5$). ^{31}P{^{1}H} NMR ($\delta$, C_6D_6): −36.3 (s).

Preparation of ZrCp"Np$_2$Cl

MgNp$_2$ (0.46 g, 2.76 mmol) dissolved in 30 ml of ether was added dropwise to ZrCp"Cl$_3$ (0.92 g, 2.76 mmol) in 60 ml of stirred ether. The color of the reaction mixture remained yellow. The magnesium chloride was filtered off and the solvent removed in vacuo from the filtrate. The resulting yellow oil would not crystallize.

^{1}H NMR (δ, C_6D_6): 1.85 (s, 15, C$_5$Me$_5$), 1.32 (s, 18, CMe$_3$), 1.00 (s, 4, CH_2-CMe$_3$).

Preparation of ZrCp"Np$_3$

ZrNp$_3$Cl (0.40 g, 1.18 mmol) and LiCp" (0.17 g, 1.18 mmol) were stirred together for 6 h in 30 ml of ether. The reaction mixture was filtered and the ether removed in vacuo from the light yellow filtrate. The resulting oily solid was extracted into a minimal amount of pentane, and the solution was cooled to −30°C to give 0.42 g (81%) of off-white crystals.

^{1}H NMR (δ, C_6D_6): 1.93 (s, 15, C$_5$Me$_5$), 1.32 (s, 27, CMe$_3$), 0.88 (s, 6, CH_2CMe$_3$).

Preparation of ZrNph$_2$Cl$_2$(TMEDA) (Nph = CH$_2$CMe$_2$Ph)

ZrNph$_2$Cl$_2$(TMEDA) was prepared in high yield (70%) using the same procedure described for the preparation of ZrNp$_2$Cl$_2$(TMEDA). LiNph is photosensitive and was recrystallized from hexane immediately before use. (It was prepared in a manner analogous to that used to prepare LiNp [14].)

Anal. Found: C, 56.51; H, 7.99; N, 5.24. ZrC$_{26}$H$_{42}$N$_2$Cl$_2$ calcd.: C, 57.33; H, 7.77; N, 5.14%. ^{1}H NMR (δ, CH$_2$Cl$_2$): 6.90—7.47 (complex, 5, Ph), 2.48 (s, 2, NCH$_2$), 2.32 (s, 6, NCH$_3$), 1.85 (s, 2, CH_2CMe$_2$Ph), 1.48 (s, 9, CMe$_2$).

Preparation of ZrBz$_2$Cl$_2$(ether)$_2$ (Bz = CH$_2$Ph)

MgBz$_2$ · 2 Et$_2$O (3.05 g, 8.6 mmol) [17] dissolved in 60 ml of ether was added dropwise to ZrCl$_4$ (2.0 g, 8.6 mmol) in 30 ml of stirred ether. The reaction mixture turned orange. It was filtered and the ether was removed in vacuo leaving 3.25 g (80%) of orange crystals. The product can be recrystallized from ether. ZrBz$_2$Cl$_2$(ether)$_2$ is photosensitive and should be prepared and stored in the dark.

^{1}H NMR (δ, C_6D_6): 6.82—7.03 (complex, 5, Ph), 3.17 (q, 4, O(CH_2CH$_3$)$_2$), 2.60 (s, 2, CH_2Ph), 0.83 (t, 6, O(CH$_2$$CH_3$)$_2$).

Preparation of ZrBz$_2$Cl$_2$L$_2$

ZrBz$_2$Cl$_2$(TMEDA) and ZrBz$_2$Cl$_2$(PMe$_3$)$_2$ were prepared in high yield (90%) by adding TMEDA or PMe$_3$ to ether solutions of ZrBz$_2$Cl$_2$(ether)$_2$. These adducts crystallize as orange needles. Recrystallization was best achieved from a toluene/ether solvent mixture.

^{1}H NMR of ZrBz$_2$Cl$_2$(TMEDA) (δ, C_6D_6): 6.95—7.07 (complex, 5, Ph), 2.55 (s, 2, CH_2Ph), 1.72 (s, 6, NCH$_3$), 1.60 (s, 2, NCH$_2$). ^{1}H NMR of ZrBz$_2$Cl$_2$-

$(PMe_3)_2$ (δ, C_6D_6): 6.95—7.07 (complex, 5, Ph), 2.63 (s, 2, CH_2Ph), 0.79 (d, 9, J(HP) 5 Hz, PMe_3).

Preparation of $[ZrCl_3(PMe_3)_2]_2$

$ZrNp_2Cl_2(PMe_3)_2$ (4.50 g, 9.86 mmol) was dissolved in 60 ml of toluene in a 125 ml Erlenmeyer flask. This solution was photolyzed for 12 h, during which time the solution turned black and forest-green, cubic crystals formed on the walls of the flask. The black solution was decanted off leaving 1.89 g (55% yield vs. Zr, 83% of theory) of $[ZrCl_3(PMe_3)_2]_2$ which was washed with toluene and dried in vacuo.

Anal. Found: C, 20.65; H, 5.21. $ZrC_6H_{18}P_2Cl_3$ calcd.: C, 20.61; H, 5.19. ^1H NMR (δ, CH_2Cl_2, $-20°C$): 1.61 (d, ^2J(HP) 6 Hz, PMe_3).

Acknowledgements

R.R.S. thanks the National Science Foundation for support (Grant CHE79-05307).

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