Hence the related η^2-iminoacyls $Cp_2M(\eta^2\text{-}ArNCCH_2Ph)(CH_2Ph)$ (M = Zr, Hf) were found to be stable for months at 100 °C in toluene. Only after 15 days at 120 °C was any reactivity detected for M = Zr, but the spectra obtained indicated a number of products being formed. Attempts to induce the 1,2-hydrogen shifts in these benzyl compounds by adding pyridine (2–10 equiv) to ^1H NMR samples followed by thermolysis failed. After days at 120 °C, essentially no decrease in the η^2-iminoacyl concentration had occurred.

The formally 16-electron derivatives **3** will undergo further reaction with a second equivalent of ArNC. However, the reaction is much slower than the first insertion and leads to the bis(amido) compounds **5**, presumable via the intermediate η^2-iminoacyl 4 (Scheme I).[16] A single-crystal X-ray diffraction study of the hafnium compound **5b**[17] confirmed both the presence of the vinylamide function as well as the trans stereochemistry about the double bond (Figure 3). The Hf–N distance of 2.182 (12) Å is longer than typically found for simple Hf(IV) amido compounds[18] and probably reflects a decrease in nitrogen p to metal d π-bonding, possibly a consequence of the metal electron configuration and the vinyl substituent on the nitrogen atom.

Mechanistic aspects of this isomerization, whether the pyridyl ring accelerates an existing pathway or introduces a new one, are presently being studied.

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Supplementary Material Available: Analytical data for new compounds and tables of additional crystal structure data, atomic and thermal parameters, H atom positions, bond distances, and bond angles (24 pages); a listing of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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[15] The compounds $Cp_2M(\eta^2\text{-}xyNCCH_2Ph)(CH_2Ph)$ (M = Zr, Hf) were formed in essentially quantitative yield by reacting the corresponding dibenzyls[2a] with xyNC. ^1H NMR (C_6D_6, 25 °C): M = Zr, δ 2.60 (s, Zr-CH_2Ph), 3.49 (s, xyNCCH_2Ph), 5.52 (s, Cp); M = Hf, δ 2.24 (s, Hf-CH_2Ph), 3.38 (s, xyNCCH_2Ph), 5.32 (s, Cp). ^{13}C NMR (C_6D_6, 25 °C): M = Zr, δ 246.5 (xyNCCH$_2$Ph); M = Hf, δ 254.1 (xyNCCH$_2$Ph).

[16] ^1H NMR (C_6D_6, 25 °C): **5a**, δ 2.10 (s, CH-py-6-*Me*), 2.45 (s, N-xy-*Me*), 5.89 (s, Cp), 4.76 (d), 9.24 (d, xyNC*H*=*CH*-py-6-Me, $^1J(^1H-^1H)$ = 13 Hz); **5b**, δ 2.15 (s, CH-py-6-*Me*), 2.50 (s, N-xy-*Me*), 5.90 (s, Cp), 4.79 (d), 9.19 (d, xyNC*H*=*CH*-py-6-Me, $^3J(^1H-^1H)$ = 12 Hz). ^{13}C NMR (C_6D_6, 25 °C): **5a**, δ 114.3 (Cp), 98.3 (xyNCH=*C*H-py-6-Me, $^1J(^{13}C-^1H)$ = 154 Hz), 135.9 (xyNCH=CH-py-6-Me, $^1J(^{13}C - ^1H)$ = 157 Hz); **5b**, δ 113.2 (Cp), 99.6 (xyN*C*H=CH-py-6-Me, $^1J(^{13}C-^1H)$ = 154 Hz), 149.2 (xyN*C*H=CH-py-6-Me, $^1J(^{13}C-^1H)$ = 166 Hz).

[17] Attempts to obtain crystals of **5b** suitable for X-ray diffraction work were frustrating. However, a few reasonably well formed samples were eventually obtained from hexane–toluene mixtures. Crystal data for $Cp_2Hf(xyNCH{=}CH\text{-}py\text{-}6\text{-}Me)_2$ (**5b**) at −155 °C: space group *I*2, a = 14.490 (7) Å, b = 8.925 (4) Å, c = 15.943 (9) Å, β = 91.03 (3)°, Z = 2, d_{calcd} = 1.262 g cm^{-3}. Of the 1464 unique intensities collected with Mo Kα radiation, $6° \leq 2\theta \leq 45°$, the 1378 having $F > 3\sigma(F)$ were used in the full-matrix refinement. There was considerable difficulty in locating several of the carbon atoms, but once located they were "well behaved". An apparent solvent molecule, toluene, was also visible in difference Fouriers and was included as a partial occupancy disordered fragment. Final residuals are R = 0.054 and R_w = 0.049.

[18] Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Abdul-Malik, K. M.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

A High Yield Route to Rhenium(VII) Bis(imido) Neopentylidene Complexes

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Summary: The reaction between $ReO_3(OSiMe_3)$ and ArNCO (Ar = 2,6-diisopropylphenyl) yields what is believed to be a mixture of $Re_2O_x(NAr)_{7-x}$ complexes, one of which, $Re_2O_2(NAr)_5$ (**1**), can be isolated in ~30% yield. Pure **1**, *or* the crude mixture, when treated with 3 equiv of py·HCl (py = pyridine) yields $Re(NAr)_2(py)Cl_3$ (**2**) in 70–80% isolated yield vs. $ReO_3(OSiMe_3)$. Addition of 0.65 equiv of $Zn(CH_2\text{-}t\text{-}Bu)_2$ to **2** yields $Re(NAr)_2(CH_2\text{-}t\text{-}Bu)Cl_2$ (**3**) in 75% isolated yield. Dehydrohalogenation of **3** with DBU yields $Re(NAr)_2(CH\text{-}t\text{-}Bu)Cl$ (**4**) virtually quantitatively, which can be treated with LiOR (OR = $OCH(CF_3)_2$ or O-2,6-C_6H_3-*i*-Pr_2) to give relatives of the type $Re(NAr)_2(CH\text{-}t\text{-}Bu)(OR)$ (**5**). Compounds **4** and **5** are very soluble, presumably monomeric, 18-electron complexes that do not react with *cis*-2-pentene or norbornene.

Rhenium is one of three metals (the others being Mo and W) that readily exhibits activity for the metathesis of olefins.[1] Although nothing is known about the type of active site in Re-based (all heterogeneous) metathesis catalyst systems, we propose that the metal is in its highest oxidation state (Re(VII) viewing the alkylidene ligand as a dianion) by analogy with now well-characterized homogeneous tungsten-based catalysts.[2] Since rhenium-based catalysts are the best so far for the matathesis of functionalized olefins,[3] the preparation of well-characterized homogeneous rhenium catalysts ultimately should prove to be of considerable practical importance, in addition to filling an important void in the chemistry of high oxidation state alkylidene and alkylidyne complexes. In view of the success we have had with tungsten complexes of the type $W(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$,[2a] we felt that a rhenium complex of the type $Re(CH\text{-}t\text{-}Bu)(NAr)_2(OR)$ was a logical target, in spite of the fact that related Re(VII) bis(*tert*-butylimido) complexes (e.g., $Re(N\text{-}t\text{-}Bu)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$) were shown to be unreactive toward olefins.[4]

The reaction between $ReO_3(OSiMe_3)$[5] and 3 equiv of ArNCO[6] in refluxing toluene for 5 h yields a mixture of at least three products, one of which can be obtained directly from the reaction in crystalline form in ~30% yield. On the basis of elemental analysis and an ^1H NMR spectrum that shows a 3:2 ratio of Ar groups, only the pair

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[1] (a) Ivin, K. J. *Olefin Metathesis*; Academic: London, 1983. (b) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8.

[2] (a) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* 1986, *108*, 2771. (b) Aguero, A.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 793.

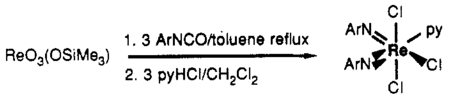
[3] (a) Mol, J. C.; Woerlee, E. F. G. *J. Chem. Soc., Chem. Commun.* **1979**, 330. (b) Verkuijen, E.; Kapteijn, F.; Mol, J. C.; Boelhouwer, C. *Ibid.* **1977**, 198.

[4] Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505.

[5] Schmidt, M.; Schmidbaur, H. *Chem. Ber.* **1959**, *92*, 2667.

[6] The reaction between an isocyanate and a metal oxide to give an imido complex has much precedent; see: Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2651 and references therein.

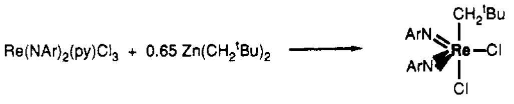
of which contains diastereotopic isopropyl methyl groups, we propose that the red product be formulated as $(\mathrm{ArN})_3\mathrm{ReORe(O)(NAr)_2}$ (1).[7] Upon addition of 3 equiv of pyridine hydrochloride to 1 in dichloromethane at 25 °C, a green product with the formula $\mathrm{Re(NAr)_2(py)Cl_3}$ (2) can be isolated in 80% yield.[7] The other products of the reaction between $\mathrm{ReO_3(OSiMe_3)}$ and ArNCO are probably variations of 1 (e.g., $\mathrm{Re_2O_3(NAr)_4}$) since the *crude* product mixture yields 2 in 75% yield upon addition of 3 equiv of py·HCl. Therefore 2 can be prepared in 75% isolated yield vs. $\mathrm{ReO_3(OSiMe_3)}$ as shown in eq 1. On the basis of ^{1}H NMR studies the imido ligands are believed to be cis in 2 with a labile pyridine ligand bound trans to one of them.



2

(1)

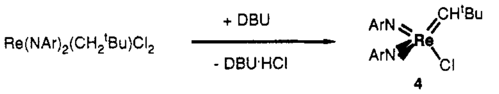
The addition of 0.65 equiv of $\mathrm{Zn(CH_2\text{-}\mathit{t}\text{-}Bu)_2}$ to 2 in dichloromethane in the presence of $\mathrm{NEt_4Cl}$ (0.65 equiv) at −30 °C yields red, crystalline $\mathrm{Re(NAr)_2(CH_2\text{-}\mathit{t}\text{-}Bu)Cl_2}$ (3) in 70% yield (eq 2) upon crystallization of the crude product from pentane.[7] The ^{1}H NMR spectrum of $\mathrm{Re(NAr)_2(CH_2\text{-}\mathit{t}\text{-}Bu)Cl_2}$ shows two types of isopropyl methyl groups to be present but only one type of methyne proton and neopentyl methylene proton. Therefore we believe 3 to be a pseudo trigonal bipyramid containing equatorial imido ligands and an axial neopentyl ligand.



3

(2)

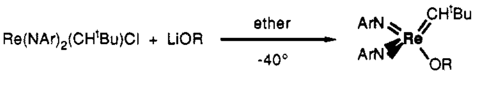
Dehydrohalogenation of 3 by 1.05 equiv of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in ether at −30 °C proceeds smoothly to give DBU·HCl and bright red, pentane-soluble $\mathrm{Re(NAr)_2(CH\text{-}\mathit{t}\text{-}Bu)Cl}$ (4) virtually quantitatively by ^{1}H NMR and in 70% isolated yield from pentane.[7] Controlled dehydrohalogenation of d^0 alkyl complexes is extremely rare.[8] In this case, we have found only DBU to be successful so far. We also have found the presence of traces of moisture to be disastrous; yellow, crystalline $\mathrm{Re(NAr)_2(O)(CH_2\text{-}\mathit{t}\text{-}Bu)}$[9] is the major product if this reaction is run on a small scale (<50 mg), we propose by attack on 4 by DBU-generated $\mathrm{OH^-}$ (from traces of water) followed by chloride loss and proton transfer from oxygen to carbon.[10]



4

(3)

The chloride ligand in 4 can be replaced by the alkoxide ligands $\mathrm{OCH(CF_3)_2}$ and O-2,6-$\mathrm{C_6H_3\text{-}\mathit{i}\text{-}Pr_2}$ (eq 4).[7] The reaction appears to be successful for the $\mathrm{OCMe(CF_3)_2}$ ligand also, but the crystalline product is too soluble to purify adequately by recrystallization from pentane. Red 5a and orange 5b are extremely soluble, moisture-sensitive species that can be crystallized (with difficulty) from pentane.



(4)

5a OR = $\mathrm{OCH(CF_3)_2}$ (45%)
5b OR = O-2,6-$\mathrm{C_6H_3{}^iPr_2}$ (65%)

Table I. Selected NMR Data for $\mathrm{Re(NAr)_2(CH\text{-}\mathit{t}\text{-}Bu)X}$ Complexes[a]

X	$\delta(\mathrm{H}_\alpha)$	$\delta(\mathrm{C}_\alpha)$	J_{CH}, Hz
Cl	12.27	269.4	136
$\mathrm{OCH(CF_3)_2}$	11.88	260.5	137
OAr	11.25	256.7	146

[a] Solvent = $\mathrm{C_6D_6}$; Ar = 2,6-$\mathrm{C_6H_3\text{-}i\text{-}Pr_2}$.

Complexes 4, 5a, and 5b all contain neopentylidene H_α signals in the range 11–12 ppm and C_α signals at ~260 ppm with $J_{\mathrm{CH}} = 135\text{–}145$ Hz (Table I). All are believed to be pseudotetrahedral monomers on the basis of their high solubility in pentane and the formal 18-electron count (if one includes the electron pair on each nitrogen atom). In each case the NAr ligands are inequivalent with four sets of isopropyl methyl groups and two types of methyne protons being observed in the ^{1}H NMR spectra. Therefore we believe that H_α of the neopentylidene ligand lies in the same plane as C_α, Re, and the N atom of one of the imido ligands and that the neopentylidene ligand is found in only one of the two possible orientations. Similar observations have been made for the $\mathrm{Re(N\text{-}\mathit{t}\text{-}Bu)_2(CH\text{-}\mathit{t}\text{-}Bu)(CH_2\text{-}\mathit{t}\text{-}Bu)}$ complex.[4]

We were disappointed to find that neither 4, nor 5a, nor 5b reacts with *cis*-2-pentene (10 equiv) or even norbornene between 25 and 65 °C in several hours.[11] Evidently "18-electron" bis(imido) complexes such as 4 or 5 (or $\mathrm{Re(N\text{-}\mathit{t}\text{-}Bu)_2(CH\text{-}\mathit{t}\text{-}Bu)(CH_2\text{-}\mathit{t}\text{-}Bu)}$) simply are not electrophilic enough. The metal–ligand bonds in Re(VII) species also should be somewhat shorter than those in W(VI) species, and the coordination sphere therefore should be more crowded, although we do not believe this factor alone to be of major import. In spite of these (and previous[4]) results, we still feel that Re(VII) is the "correct" oxidation state in rhenium metathesis catalysts. Possibly neutral Re(VII) alkylidene complexes may never be electrophilic enough to react with ordinary olefins, so we also will be searching for a route to a cationic,[12] preferably four-coordinate complex containing only one imido ligand. We hope to find a route that utilizes the facile entry into Re(VII) chemistry reported here.

Acknowledgment. R.R.S. thanks the National Science Foundation for support through Grant CHE 84-02892.

Supplementary Material Available: Full preparative details and analytical and NMR data for compounds 1–5 (5 pages). Ordering information is given on any current masthead page.

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(7) Full preparative details and analytical and NMR data are available as supplementary material.

(8) (a) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359. (b) Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483.

(9) IR (Nujol); 907 cm^{-1} (ν_{ReO}); see supplementary material.

(10) (a) We have encountered other reactions that most likely involve transfer of a proton from MOH to an unsaturated carbon atom in a metal–carbon bond.[10b–d] (b) Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1982**, *1*, 1332. (c) Feinstein-Jaffe, I.; Gibson, D.; Lippard, S. J.; Schrock, R. R.; Spool, A. *J. Am. Chem. Soc.* **1984**, *106*, 6305. (d) Feinstein-Jaffe, I.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 1189.

(11) Polynorbornene is sometimes observed, but the rate and amount are variable, and no new signal for the expected new alkylidene α-proton is ever observed. We believe that polymer is formed by a more active impurity, perhaps a hydrolysis product.

(12) (a) Osborn[12b,c] has good evidence that four-coordinate cationic complexes of the type $[\mathrm{W(CH\text{-}\mathit{t}\text{-}Bu)(OR)_2X}]^+$ (X = a halide) are extremely active catalysts for the metathesis of ordinary olefins. (b) Kress, J.; Wesolek, M.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 514. (c) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6346.