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A series of mono- and dihydrido- as well as mono- and dimethylosmium(II) complexes containing [(mes)Os(CNR)] as a building block

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Dedicated to Professor Fausto Calderazzo, a good friend and a creative scientist, on the occasion of his 70th birthday.

Abstract

The dihydridoosmium(II) complexes [(mes)OsH$_2$(CNR)] (**7**–**10**) were prepared in excellent yield from the dichloroosmium(II) precursors [(mes)OsCl$_2$(CNR)] upon treatment with 10% magnesium amalgam in THF in the presence of ethanol. Under similar conditions, the methylisocyanide derivative [(mes)OsH$_2$(CNMe)] (**6**) as well as the monohydrido compounds [(mes)OsH(X)(CNMe)] (**11**, **13**) were obtained. The same methodology using [(mes)OsCl(C$_6$H$_5$)(CNR)] as the starting material was applied for the preparation of the hydrido(phenyl)osmium(II) complexes [(mes)OsH(C$_6$H$_5$)(CNR)] (**19**–**23**) which were also isolated in almost quantitative yield. Treatment of these complexes with HCl in CH$_2$Cl$_2$ at -78°C led to the cleavage of the osmium–phenyl but not the osmium–hydride bond. Reactions of [(mes)OsCl$_2$(CNR)] with MeLi/LiCl gave exclusively the dimethylosmium(II) compounds [(mes)Os(CH$_3$)$_2$(CNR)] (**29**–**32**) while the corresponding reactions with MeLi/LiI afforded a mixture of **29**–**32** and the monomethyl derivatives [(mes)OsI(Me)(CNR)] (**26**, **33**–**35**). A cyclic carbeneosmium(II) complex **37** was obtained from [(mes)OsCl$_2$(CNPh)] and MeLi/LiI followed by treatment with deactivated Al$_2$O$_3$. The etheneosmium(0) compound [(mes)Os(C$_2$H$_4$)(CNMe)] (**38**) was prepared from the dimethylosmium(II) precursor **29** and briefly investigated as starting material for photochemical C–H activation reactions. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Osmium; Arene complexes; Isocyanide complexes; Hydrido complexes; Alkyl complexes; C–H activation

1. Introduction

Some years ago, we described a new family of mesityleneosmiumcarbonyl complexes in which the [(mes)Os(CO)] fragment (mes = mesitylene = 1.3.5-trimethylbenzene) was linked to two formally anionic ligands such as H, Cl, Br, I, CH$_3$, C$_6$H$_5$ and other C-bonded units [1–3]. The aim of these studies was to find out whether 18-electron compounds of the general composition [(mes)OsX(X′)(CO)] are stable and usable as precursors to generate 16-electron species [(mes)Os(CO)] which, like the structurally related [(C$_5$R$_5$)Ir(CO)] counterpart [4], could be a candidate for activating C–H bonds. Based on a collaboration with the Perutz group, an account of this work has already appeared [5].

Taking the similar σ-donor/π-acceptor capabilities of CO and CNR into consideration, we started a program to prepare a series of halfsandwich-type mesityleneosmium(II) complexes in which apart from halide, hydride, alkyl and aryl groups also various isocyanides are coordinated to the metal center. In two recent articles we described the preparation of the dichloro compounds [(mes)OsCl$_2$(CNR)] (R = Me, *t*Bu, Ph, Cy, Xyl) and their reactions with some organolithium and Grignard reagents [6,7]. Moreover, we reported about the synthesis and vibrational analysis of the dihydridoosmium(II) derivative [(mes)OsH$_2$(CNMe)] which was obtained from [(mes)OsCl$_2$(CNMe)] and Mg/Hg in THF in the presence of ethanol as a proton source [8]. The present paper is not only an extension of this work but it also describes the preparation of a series of monohydridoosmium(II) complexes [(mes)OsH(X)(CNR)] with X = Cl, Br, I and Ph as well as of related mono- and dimethylosmium(II) counter-

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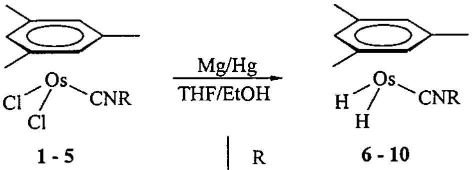
parts. Some preliminary results on intra- and intermolecular C–H activation reactions of the etheneosmium(0) derivative [(mes)Os(C_2H_4)(CNMe)] will also be discussed.

2. Results and discussion

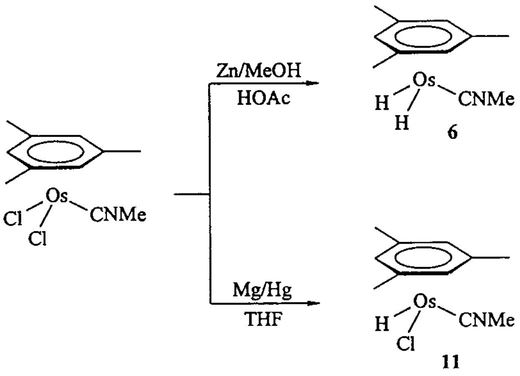
The synthesis of the formerly unknown dihydridoosmium(II) complexes **7**–**10** followed the route which we already described for the analogous compound **6**. Treatment of the dichloroosmium(II) precursors **2**–**5** (Scheme 1) with a slurry of magnesium amalgam (10% of Mg) in THF and a small amount of ethanol gave after workup and recrystallization from CH_2Cl_2–hexane or sublimation in vacuo the OsH_2 derivatives **7**–**10** in almost quantitative yield. The off-white solids, which are soluble in all common organic solvents, were characterized by elemental analysis, mass spectra and IR as well as NMR spectroscopic techniques. The most typical feature of the NMR spectra is the high-field resonance for the hydrido ligands in the ^{1}H-NMR which appears between δ −10.00 and −10.25 as a singlet. With regard to the reactivity of various hydridometal compounds toward chloroform and other halocarbons [9] we note that solutions of **6** in $CHCl_3$ and CH_2Cl_2 are stable for ca. 20 h without decomposition.

An alternative method for the preparation of the dihydrido complex **6** with methylisocyanide as co-ligand consists in the reaction of **1** with an excess of zinc dust in methanol in the presence of glacial acetic acid (Scheme 2). After chromatographic separation of the products, compound **6** was isolated in 63% yield. If the starting material **1** was treated with Mg/Hg in THF in the absence of ethanol, instead of the dihydrido complex **6** the corresponding chloro(hydrido)osmium(II) derivative **11** was formed in moderate yield. Although we cannot exclude that traces of water were present in the reaction system, we assume that for the generation of **11** the solvent THF behaves as the proton source. Earlier observations by S. Stahl are in agreement with this hypothesis [10].



	R
1, 6	Me
2, 7	*t*Bu
3, 8	Ph
4, 9	Cy
5, 10	Xyl

Scheme 1.

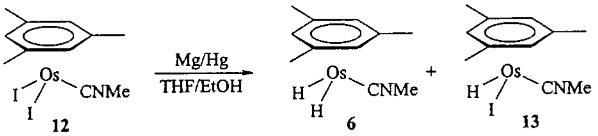


Scheme 2.

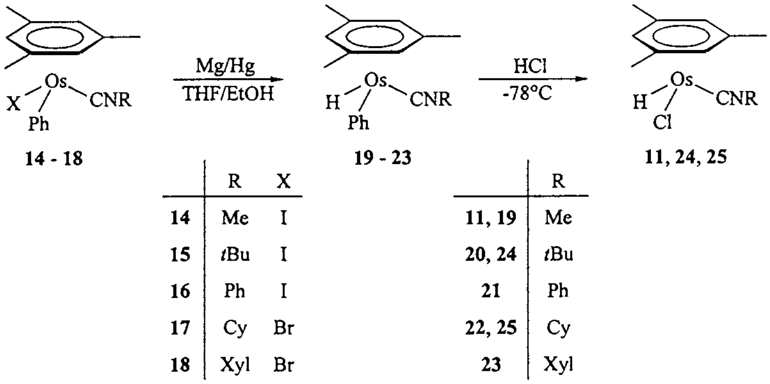
The hydrido(iodo)osmium(II) complex **13**, which can be considered as a counterpart of compound **11**, was obtained as a byproduct in the reaction of the diiodo derivative **12** with Mg/Hg in THF/EtOH (Scheme 3). The ^{1}H-NMR spectrum of **13**, which like **11** is a yellow air-sensitive solid, displays the hydride resonance at δ −10.00 and thus in the same region as the related dihydrido complex. In contrast, the ^{1}H-NMR spectrum of **11** exhibits the signal of the metal-bonded hydrogen at δ −8.27.

The bromo- and iodo(phenyl)osmium(II) compounds **14**–**18**, which are readily accessible from the dichloro derivatives **1**–**5** upon treatment with either PhMgBr or PhMgI [6,7], also react with magnesium amalgam in THF in the presence of ethanol to afford the hydrido(phenyl) complexes **19**–**23** in nearly quantitative yield. While **19** and **23** are yellow, modestly air-sensitive solids, the analogous compounds **20**–**22** are yellow oils which like the analogous mono- and dihydrido derivatives **6**–**11** and **13** are soluble in all common organic solvents. The relevant spectroscopic data of **19**–**23** (i.e. the C≡N stretching vibration in the IR, the hydride resonance in the ^{1}H-NMR and the signal for the *C*NR nuclei in the ^{13}C-NMR spectra) are similar to those of the other hydridoosmium(II) complexes prepared in this work and thus deserve no further comments.

The reactivity of the new $OsH(C_6H_5)$ derivatives toward HCl was studied using **19**, **20** and **22** as examples. The crucial question was whether the attack of the electrophile would lead preferentially to a cleavage of the Os–H or the Os–C_6H_5 bond. The answer is clear: if a slow stream of dry HCl was passed through a solution of **19**, **20** or **22** in CH_2Cl_2 at −78°C, a rapid reaction occurred which gave the chloro(hy-



Scheme 3.



	R	X
14	Me	I
15	*t*Bu	I
16	Ph	I
17	Cy	Br
18	Xyl	Br

	R
11, 19	Me
20, 24	*t*Bu
21	Ph
22, 25	Cy
23	Xyl

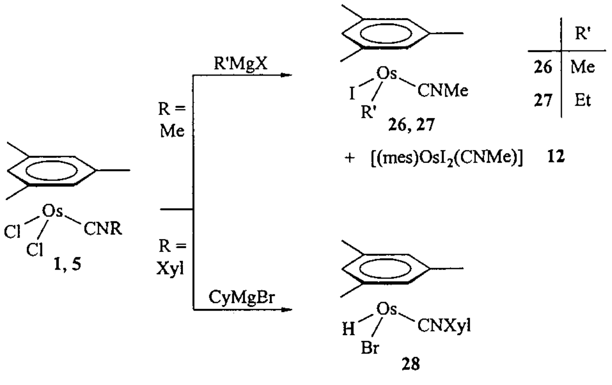
Scheme 4.

drido)osmium(II) complexes **11**, **24** and **25** in 90–95% isolated yield (see Scheme 4). Under the chosen conditions, neither the Os–H nor the Os–CNR bond are attacked by the proton source. Therefore, the isocyanide compounds **19**, **20** and **22** behave similarly to the carbonyl derivative [(mes)OsH(C_6H_5)CO] which reacts with HCl to form [(mes)OsHCl(CO)] and not [(mes)OsCl(C_6H_5)(CO)] [11].

The bromo(hydrido)osmium(II) complex **28** containing CNXyl as the isocyanide ligand was obtained on an unexpected route. After we found that compound **1** reacted with both CH_3MgI and C_6H_5MgI to give a mixture of [(mes)OsI(R′)(CNMe)] (R′ = Me, Ph) and [(mes)OsI_2(CNR)] [6], we studied also the reactivity of **1** and **5** toward other Grignard reagents. Treatment of **1** with C_2H_5MgI in ether gave, apart from **12** as the main product, small amounts of the ethyl(iodo)osmium(II) derivative **27** (Scheme 5), which was isolated as an orange–yellow solid in 6% yield. Even with an excess of C_2H_5MgI, the bis(ethyl) complex [(mes)Os(C_2H_5)$_2$(CNMe)] could not be obtained. The reaction of the xylylisocyanide complex **5** with $C_6H_{11}MgBr$ led instead of a mono- or bis(alkyl)osmium(II) compound to the bromo(hydrido) complex **28** in 70% yield. Since we observed the formation of cyclohexene as a byproduct, it is conceivable that **28** is generated via a β-hydride shift from the supposed bromo(cyclohexyl)osmium(II) species [(mes)OsBr(C_6H_{11})(CNXyl)] as an intermediate. The ^{1}H-NMR spectrum of **28** exhibits the hydride signal at δ −8.78, i.e. with a chemical shift between that of **11** and **13**.

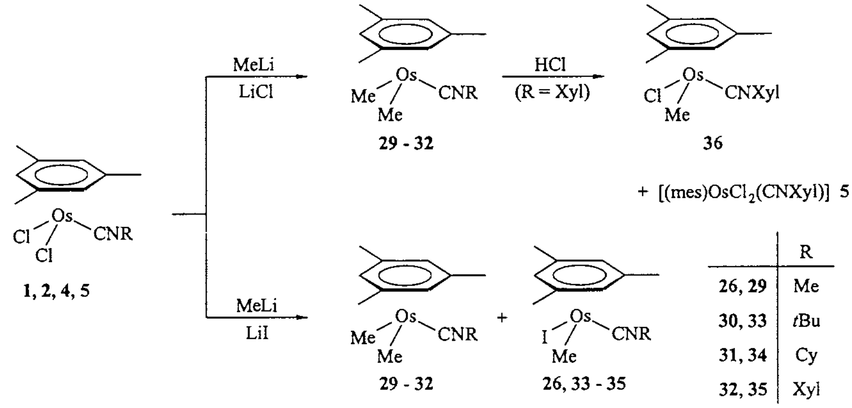
The results covering the reactivity of the dichloroosmium(II) complexes **1**, **2**, **4** and **5** toward methyllithium are summarized in Scheme 6. The important point is that the course of the reaction depends on the starting material from which MeLi is generated. If CH_3Cl is used, the reagent consists of a mixture of MeLi and LiCl and under these conditions the dimethylosmium(II) compounds **29**–**32** are formed as the dominating products in good to excellent yield. In this case, the formation of the corresponding monomethyl derivatives [(mes)OsCl(CH_3)(CNR)] could not be detected. In contrast, if the methyllithium is generated from CH_3I and, therefore, the solution contains apart from MeLi also LiI, a mixture of both the dimethyl- and the iodo(methyl)osmium(II) complexes is obtained. The yield of the latter (**26** and **33**–**35**) is about 30–40%. Similar observations had been made with [(mes)Os(CO)Cl_2] as the starting material which upon treatment with MeLi/LiI also gave a mixture of [(mes)Os(CH_3)$_2$(CO)] and [(mes)OsI(CH_3)(CO)], respectively [1b].

The dimethylosmium(II) compounds **29**–**32** are yellow air-sensitive solids which are readily soluble in organic solvents and can be sublimed in vacuo. In solution (particularly in $CHCl_3$ and CH_2Cl_2), even under argon, slow decomposition occurs. The ^{1}H-NMR spectra of **29**–**32** display the signal for the $OsCH_3$ protons at δ 0.86–0.93 and thus significantly upfield compared with the iodo(methyl) derivatives **26** [6] and **33**–**35** (δ 1.62–1.74). In the ^{13}C-NMR spectra of **29** and **32** the resonance of the methylcarbon nuclei appears also at relatively high field (δ −21.7 and −20.5, respectively). We note that although among the products of the reaction of **1**, **2**, **4** and **5** with MeLi/LiCl the monomethyl complexes [(mes)OsCl(CH_3)(CNR)] were



	R'
26	Me
27	Et

Scheme 5.



Scheme 6.

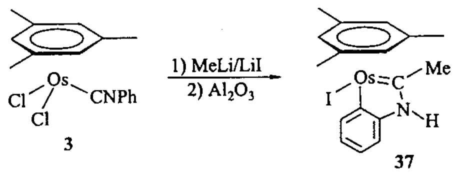
not observed, the xylylisocyanide compound **32**, which was taken as an example, reacts with HCl in CH_2Cl_2 at -78°C to give apart from [(mes)$OsCl_2$(CNXyl)] (**5**) also the chloro(methyl) derivative **36** as a minor product.

The phenylisocyanide complex **3** behaves differently toward methyllithium than the other compounds of the general composition [(mes)$OsCl_2$(CNR)] (see Scheme 7). If a suspension of **3** in benzene is treated with a solution of MeLi/LiI in ether and the reaction mixture worked up by chromatographic techniques, an orange–red solid is isolated the analytical composition of which corresponds to [(mes)OsI(CH_3)(CNPh)]. The spectroscopic data reveal, however, that the compound is not an isocyanideosmium(II) derivative but instead the cyclic carbene complex **37** containing an *ortho*-metalated phenyl ring. The most characteristic features in the ^{1}H-NMR spectrum of **37** are the NH resonance at δ 10.00 and the pattern for the C_6H_4 protons consisting of three signals at δ 7.73, 7.01 and 6.71 with the intensity ratio 1:1:2. The ^{13}C-NMR spectrum of **37** exhibits a low-field resonance at δ 230.0, which is typical for the carbene carbon atom of aminocarbene complexes of this type [6,7]. In this context it should be mentioned that compound **3** reacts with PhLi to give a mixture of products among which is a relative of **37** containing two phenyl groups linked to the metal and the carbene carbon atom. This complex was characterized by an X-ray crystal structure analysis [7].

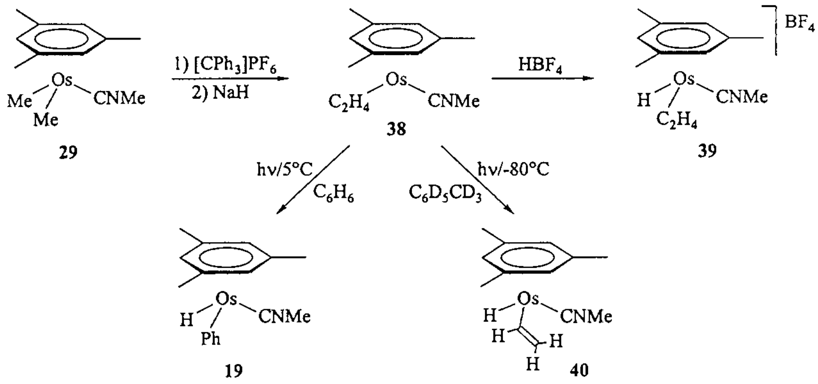
The dimethylosmium(II) compound **29** can be employed as the starting material for the preparation of the ethene(isocyanide)osmium(0) complex **38** (Scheme 8). Following earlier work from our laboratory about the synthesis of ethenemetal derivatives [M(C_2H_4)L_n] from dimethylmetal precursors [M$(CH_3)_2L_n$] [12,13], we found that stepwise treatment of **29** with an equimolar amount of [CPh_3]PF_6 in CH_2Cl_2 and subsequent reaction with NaH in THF gave the osmium(0) compound **38** as a yellow air-sensitive solid in moderate yield. There is spectroscopic evidence that in the initial step of this process a cationic intermediate [(mes)OsH(C_2H_4)(CNMe)]$^+$ is generated together with some byproducts possibly formed via attack of the electrophile at the isocyanide ligand. The BF_4 salt **39** (a yellow–brown, extremely air-sensitive solid) of the supposed intermediate was obtained by protonation of **38** with HBF_4 and characterized by spectroscopic means.

Taking into consideration that the photochemistry of halfsandwich-type complexes [(η^5-C_5R_5)M(L)(L′)] (M = Rh, Ir) [4,14,15] and [(η^6-C_6R_6)M′(L)(L′)] (M′ = Ru, Os) [5,16], where the ligands L and L′ were CO, C_2H_4, PMe_3, P*i*Pr_3, etc., provided an excellent opportunity to develop routes for the inter- and intramolecular activation of C–H bonds [17], the photochemical behavior of compound **38** was briefly investigated. Irradiation of **38** in benzene at 5°C for 2 h results in the elimination of ethene and the generation of the hydrido(phenyl)osmium(II) complex **19** which was first prepared from **14** by iodide/hydride exchange (see Scheme 4). During the photolysis of **38** in benzene at 5°C, small amounts of free mesitylene were equally formed. We note that Jones and Feher reported that the bis(isocyanide)rhodium(I) derivative [(η^5-C_5Me_5)Rh($CNCH_2CMe_3$)$_2$] produces the imine PhCH=NCH_2CMe_3 upon irradiation in benzene possibly via the hydrido(phenyl)rhodium(III) intermediate [(η^5-C_5Me_5)RhH(C_6H_5)($CNCH_2CMe_3$)] [18]. In our system, an analogous C–C coupling reaction has not been observed.

In contrast to the photochemical reaction of **38** in benzene at 5°C resulting in an intermolecular C–H activation, irradiation of **38** in toluene-d_8 at -85°C



Scheme 7.



Scheme 8.

leads to an isomerization of the starting material to give **40**. The ^{1}H-NMR spectrum of **40** displays the hydride resonance at δ -9.71 while the signal pattern for the vinyl protons appears at δ 8.40, 6.85 and 5.83, respectively. As expected from recent investigations of related hydrido(vinyl) metal complexes [5,14–16,19], compound **40** is stable in solution at room temperature (r.t.) and does not isomerize back to **38** under ambient conditions. Likewise to the behavior of **19**, an insertion of the isocyanide ligand into the vinyl–osmium bond of **40** does not occur.

3. Experimental

All experiments were carried out under an atmosphere of argon by using Schlenk techniques. The starting materials **1**–**5**, **12**, and **14**–**18** were prepared according to published methods [6,7]. IR: Perkin–Elmer 1320. NMR: Jeol FX 90Q, Bruker AMX 400. Mass spectra: Finnigan 90 MAT and 8200 MAT. Melting and decomposition points were determined by DTA.

3.1. Preparation of [(mes)OsH$_2$(CNR)] (7–10)

A suspension of 0.22 mmol of the starting material **2**–**5** in 5 ml of THF was added dropwise to a slurry of 10% magnesium amalgam (formed from 25.0 mg of Mg and 2.0 g of Hg) in 5 ml of THF and 0.1 ml of EtOH. After the mixture was vigorously stirred for 1 h at r.t., the solution was decanted and the residue was washed twice with 10 ml of THF. The combined solutions were evaporated to dryness in vacuo, the remaining oily residue was extracted three times with 10 ml of benzene each, and the solvent was removed from the extracts. An off-white solid was obtained, which was either recrystallized from dichloromethane–hexane or sublimed in vacuo (60°C/5 × 10^{-5} mbar). On this route, the methylisocyanide complex **6** had also been prepared [6].

7: Yield 81 mg (93%), m.p. 102°C (dec.). Anal. Found: C, 42.76; H, 6.10; N, 3.65. Calc. for $C_{14}H_{23}NOs$: C, 42.51; H, 5.86; N, 3.54%. MS (70 eV): *m*/*z* 397 (1, M^+), 395 (2, $M^+ - H_2$). IR (CH_2Cl_2): ν(CN), ν(OsH) 2101, 2056 cm^{-1}. ^{1}H-NMR (C_6D_6, 90 MHz): δ 4.88 (s, 3H, C_6H_3 of mes), 2.32 (s, 9H, C_6Me_3 of mes), 1.07 (s, 9H, *t*Bu), -10.24 (s, 2H, OsH_2).

8: Yield 83 mg (91%), m.p. 100°C (dec.). Anal. Found: C, 46.48; H, 4.58; N, 3.64. Calc. for $C_{16}H_{19}NOs$: C, 46.25; H, 4.61; N, 3.37%. MS (70 eV): *m*/*z* 415 (0.1, $M^+ - H_2$). IR (CH_2Cl_2): ν(CN), ν(OsH) 2057, 2003 cm^{-1}. ^{1}H-NMR (C_6D_6, 90 MHz): δ 6.98 (m, 5H, C_6H_5), 4.91 (s, 3H, C_6H_3 of mes), 2.25 (s, 9H, C_6Me_3 of mes), -10.01 (s, 2H, OsH_2).

9: Yield 84 mg (90%), m.p. 74°C (dec.). Anal. Found: C, 45.79; H, 6.28; N, 3.27. Calc. for $C_{16}H_{25}NOs$: C, 45.48; H, 5.98; N, 3.32%. MS (70 eV): *m*/*z* 423 (0.1, M^+), 421 (0.1, $M^+ - H_2$). IR (CH_2Cl_2): ν(CN), ν(OsH) 2084, 2062 cm^{-1}. ^{1}H MNR (C_6D_6, 90 MHz): δ 4.90 (s, 3H, C_6H_3 of mes), 3.33 (m, 1H, CH of C_6H_{11}), 2.34 (s, 9H, C_6Me_3 of mes), 1.25 (m, 10H, CH_2 of C_6H_{11}), -10.25 (s, 2H, OsH_2).

10: Yield 91 mg (93%), m.p. 119°C (dec.). Anal. Found: C, 48.70; H, 5.27; N, 3.10. Calc. for $C_{18}H_{23}NOs$: C, 48.74; H, 5.23; N, 3.16%. MS (70 eV): *m*/*z* 445 (14, M^+), 443 (17, $M^+ - H_2$). IR (CH_2Cl_2): ν(CN), ν(OsH) 2055, 1998 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 6.74 (s, 3H, C_6H_3 of Xyl), 4.92 (s, 3H, C_6H_3 of mes), 2.32 (s, 6H, C_6Me_2 of Xyl), 2.29 (s, 9H, C_6Me_3 of mes), -10.01 (s, 2H, OsH_2). ^{13}C-NMR (C_6D_6, 100.6 MHz): δ 161.3 (s, *C*NXyl), 134.3 (s, *C*CH$_3$ of Xyl), 132.1 (s, *ipso*-C of Xyl), 127.8, 125.0 (both s, CH of Xyl), 99.1 (s, *C*CH$_3$ of mes), 79.2 (s, CH of mes), 21.4 (s, CH$_3$ of mes), 19.3 (s, CH$_3$ of Ph and Xyl).

3.2. Alternative preparative procedure for [(mes)OsH$_2$(CNMe)] (6)

A suspension of 105 mg (0.25 mmol) of **1** in 15 ml of methanol and 1.5 ml of acetic acid (99%) was treated with excess of zinc dust (ca. 200 mg) and stirred for 4 h at r.t. The solvent was removed in vacuo, the residue was extracted with 2 ml of benzene and the solution was chromatographed on Al_2O_3 (basic, activity grade III, height of column 5 cm). With benzene, a pale yellow fraction was eluted which after it was brought to dryness in vacuo gave an off-white solid. Yield 55 mg (63%).

3.3. Preparation of [(mes)OsHCl(CNMe)] (**11**)

This compound was prepared analogously as described for **7**–**10** from 95 mg (0.22 mmol) of **1**, but in the absence of ethanol. After recrystallization from dichloromethane–hexane a light yellow solid was obtained. Yield 40 mg (47%), m.p. 155°C (dec.). Anal. Found: C, 33.86; H, 4.07; N, 3.38. Calc. for $C_{11}H_{16}ClNOs$: C, 34.06; H, 4.16; N, 3.61%. MS (70 eV): *m*/*z* 389 (4, M^+), 353 (7, $M^+ - HCl$). IR (CH_2Cl_2): ν(CN) 2158, ν(OsH) 2039 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 4.57 (s, 3H, C_6H_3 of mes), 2.42 (s, 3H, CNMe), 2.08 (s, 9H, C_6Me_3 of mes), -8.27 (s, 1H, OsH).

3.4. Preparation of [(mes)OsHI(CNMe)] (**13**)

This compound was prepared analogously as described for **7**–**10**, using 133 mg (0.22 mmol) of **12** and 10% Mg/Hg in THF/EtOH as starting materials. After the crude product was extracted from the reaction mixture with benzene, the extract was concentrated to ca. 2 ml in vacuo and the solution was then chromatographed on Al_2O_3 (basic, activity grade III, height of column 5 cm). With hexane, a pale yellow fraction was eluted which contained the dihydrido complex **6**; yield 51 mg (65%). Subsequently, with benzene a yellow fraction was eluted from which after removal of the solvent a yellow solid **13** was obtained; yield 27 mg (26%), m.p. 124°C (dec.). Anal. Found: C, 27.86; H, 3.38; N, 2.70. Calc. for $C_{11}H_{16}INOs$: C, 27.56; H, 3.36; N, 2.92%. MS (70 eV): *m*/*z* 481 (15, M^+), 439 (8, $M^+ - H - CNMe$), 354 (3, $M^+ - I$). IR (CH_2Cl_2): ν(CN) 2151, ν(OsH) 2043 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 4.63 (s, 3H, C_6H_3 of mes), 2.54 (s, 3H, CNMe), 2.08 (s, 9H, C_6Me_3 of mes), -8.27 (s, 1H, OsH).

3.5. Preparation of [(mes)OsH(C_6H_5)(CNR)] (**19**–**23**)

A solution of 0.20 mmol of the starting material **14**–**18** in 5 ml of THF was added dropwise to a slurry of 10% magnesium amalgam (formed from 25.0 mg of Mg and 2.0 g of Hg) in 5 ml of THF and 0.1 ml of EtOH. After the mixture was stirred for 1.5 h, the solution was decanted and the residue was washed twice with 10 ml of THF. The combined solutions were evaporated to dryness in vacuo, the oily residue was extracted twice with 10 ml of 1:1 hexane–benzene, and the solvent was removed from the extracts. In the case of **19** and **23** yellow microcrystalline solids, while in the case of **20**–**22** yellow oils were obtained.

19: Yield 76 mg (88%), m.p. 83°C (dec.). Anal. Found: C, 47.80; H, 4.98; N, 3.25. Calc. for $C_{17}H_{21}NOs$: C, 47.53; H, 4.93; N, 3.26%. MS (70 eV): *m*/*z* 431 (1, M^+), 354 (1, $M^+ - C_6H_5$), 3.53 (1, $M^+ - C_6H_6$). IR (CH_2Cl_2): ν(CN), ν(OsH) 2116 (br) cm^{-1}. ^{1}H-NMR (C_6D_6, 90 MHz): δ 7.98 (m, 2H, C_6H_5), 7.16 (m, 3H, C_6H_5), 4.66 (s, 3H, C_6H_3 of mes), 2.43 (s, 3H, CNMe), 2.01 (s, 9H, C_6Me_3 of mes), -9.38 (s, 1H, OsH).

20: Yield 83 mg (88%), yellow oil. Anal. Found: C, 51.28; H, 5.81; N, 2.95. Calc. for $C_{20}H_{27}NOs$: C, 50.93; H, 5.77; N, 2.97%. MS (70 eV): *m*/*z* 473 (5, M^+), 395 (7, $M^+ - C_6H_6$), 312 (3, $M^+ - C_6H_6 - CN\textit{t}Bu$). IR ($CH_2Cl_2$): ν(CN), ν(OsH) 2101, 2064 cm^{-1}. ^{1}H-NMR (C_6D_6, 90 MHz): δ 7.95 (m, 2H, C_6H_5), 7.16 (m, 3H, C_6H_5), 4.64 (s, 3H, C_6H_3 of mes), 2.01 (s, 9H, C_6Me_3 of mes), 1.02 (s, 9H, *t*Bu), -9.33 (s, 1H, OsH).

21: Yield 86 mg (88%), yellow oil. Anal. Found: C, 54.28; H, 4.81; N, 2.95. Calc. for $C_{22}H_{23}NOs$: C, 53.75; H, 4.72; N, 2.85%. MS (70 eV): *m*/*z* 493 (4, M^+), 415 (7, $M^+ - C_6H_6$). IR (CH_2Cl_2): ν(CN), ν(OsH) 2061, 2019 cm^{-1}. ^{1}H-NMR (C_6D_6, 90 MHz): δ 8.00 (m, 4H, C_6H_5), 6.83 (m, 6H, C_6H_5), 4.68 (s, 3H, C_6H_3 of mes), 1.97 (s, 9H, C_6Me_3 of mes), -9.19 (s, 1H, OsH).

22: Yield 87 mg (87%), yellow oil. Anal. Found: C, 53.53; H, 6.22; N, 2.74. Calc. for $C_{22}H_{29}NOs$: C, 53.09; H, 5.87; N, 2.81%. MS (70 eV): *m*/*z* 499 (42, M^+), 421 (55, $M^+ - C_6H_6$), 390 (100, $M^+ - CNCy$), 389 (83, $M^+ - H - CNCy$), 312 (26, $M^+ - C_6H_6 - CNCy$). IR (CH_2Cl_2): ν(CN), ν(OsH) 2109, 2104 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 7.99 (m, 2H, C_6H_5), 7.13 (m, 3H, C_6H_5), 4.67 (s, 3H, C_6H_3 of mes), 3.25 (m, 1H, C_6H_{11}), 2.04 (s, 9H, C_6Me_3 of mes), 1.38 (m, 6H, C_6H_{11}), 0.95 (m, 4H, C_6H_{11}), -9.30 (s, 1H, OsH). ^{13}C-NMR (C_6D_6, 100.6 MHz): δ 147.9 (s, *C*NCy), 146.4, 145.5, 126.6, 121.3 (all s, C_6H_5), 100.9 (s, *C*CH_3 of mes), 78.2 (s, CH of mes), 53.7 (s, CH of C_6H_{11}), 34.0, 25.4, 23.1, (all s, CH_2 of C_6H_{11}), 20.1 (s, CH_3 of mes).

23: Yield 96 mg (92%), m.p. 95°C (dec.). Anal. Found: C, 55.74; H, 5.29; N, 2.76. Calc. for $C_{24}H_{27}NOs$: C, 55.47; H, 5.24; N, 2.70%. MS (70 eV): *m*/*z* 521 (12, M^+), 443 (5, $M^+ - C_6H_6$). IR (CH_2Cl_2): ν(CN), ν(OsH) 2059, 2024 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 7.98 (m, 2H, C_6H_5), 7.11 (m, 3H, C_6H_5), 6.69 (s, 3H, C_6H_3 of Xyl), 4.70 (s, 3H, C_6H_3 of mes), 2.18 (s, 6H, C_6Me_2 of Xyl), 2.01 (s, 9H, C_6Me_3 of mes), -9.18 (s, 1H, OsH). ^{13}C-NMR (C_6D_6, 100.6 MHz): δ 159.6 (s, *C*NXyl), 145.6, 143.9, 134.5, 131.4, 127.7, 126.9, 125.4, 121.6 (all s, ring-C of Xyl) 102.8 (s, *C*CH_3 of mes), 80.1 (s, CH of mes), 20.2 (s, CH_3 of mes), 19.0 (s, CH_3 of Xyl).

*3.6. Preparation of [(mes)OsHCl(CNR)] (**11**, **24**, **25**) from **19**, **20**, **22***

A slow stream of dry HCl was passed through a solution of 0.20 mmol of **19**, **20** or **22** in 5 ml of CH_2Cl_2 for 30 s at −78°C. The solvent was removed, the residue was dissolved in 2 ml of benzene and the solution was chromatographed on Al_2O_3 (basic, activity grade III, height of column 5 cm). With 1:2 C_6H_6–CH_2Cl_2 a yellow fraction was eluted which was evaporated to dryness in vacuo. The remaining yellow solid was washed twice with 1 ml of pentane (−30°C) and dried. With **19** as the starting material, compound **11** was obtained; yield 73 mg (94%).

24: Yield 78 mg (91%), m.p. 106°C (dec.). Anal. Found: C, 39.54; H, 5.18; N, 3.15. Calc. for $C_{14}H_{22}ClNOs$: C, 39.11; H, 5.16; N, 3.26%. MS (70 eV): *m*/*z* 431 (25, M^+), 347 (28, $M^+ - H - CN\textit{t}Bu$), 339 (100, (mes)$OsHCN^+$), 312 (14, (mes)Os^+). IR (CH_2Cl_2): ν(CN), ν(OsH) 2125 (br) cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 4.59 (s, 3H, C_6H_3 of mes), 2.10 (s, 9H, C_6Me_3 of mes), 1.05 (s, 9H, *t*Bu), −8.28 (s, 1H, OsH). ^{13}C-NMR (C_6D_6, 100.6 MHz): δ 136.9 (s, *C*N*t*Bu), 99.2 (s, *C*CH_3 of mes), 76.7 (s, CH of mes), 56.4 (s, *C*CH_3 of *t*Bu), 31.1 (s, CH_3 of *t*Bu), 19.9 (s, CH_3 of mes).

25: Yield 85 mg (93%), m.p. 114°C (dec.). Anal. Found: C, 41.82; H, 5.03; N, 3.03. Calc. for $C_{16}H_{24}ClNOs$: C, 42.14; H, 5.30; N, 3.07%. MS (70 eV): *m*/*z* 457 (5, M^+), 422 (2, $M^+ - HCl$), 347 (5, $M^+ - H - CNCy$), 312 (2, (mes)Os^+). IR (CH_2Cl_2): ν(CN), ν(OsH) 2130, 2048 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 4.60 (s, 3H, C_6H_3 of mes), 3.35 (m, 1H, CH of C_6H_{11}), 2.12 (s, 9H, C_6Me_3 of mes), 1.53 (m, 2H, C_6H_{11}), 1.37 (m, 4H, C_6H_{11}), 1.02, 0.93 (both m, 2H each, C_6H_{11}), −8.21 (s, 1H, OsH).

*3.7. Preparation of [(mes)OsI(C_2H_5)(CNMe)] (**27**)*

This was carried out analogously as described for **26** [6]: a suspension of 150 mg (0.36 mmol) of **1** in 10 ml of benzene was treated at 5°C with 2.2 ml of a 0.25 M solution (0.55 mmol) of C_2H_5MgI in ether. After warming to r.t., the reaction mixture was stirred for 30 min, and then ca. 100 mg of basic Al_2O_3 was added. The solvent was removed in vacuo, the residue was extracted with 3 ml of 1:1 C_6H_6–CH_2Cl_2 and the extract was chromatographed on Al_2O_3 (basic, activity grade III, height of column 4 cm). With benzene an orange fraction and with dichloromethane a red fraction were eluted. From the latter, a red solid was isolated after removal of the solvent and identified as **12** by comparison of the spectroscopic data with those of an authentic sample [6]; yield 200 mg (92%). From the orange fraction, an orange–yellow solid **27** was obtained; yield 10 mg (6%). Anal. Found: C, 31.09; H, 4.55; N, 2.35. Calc. for $C_{13}H_{20}INOs$: C, 30.77; H, 3.97; N, 2.76%. MS (70 eV): *m*/*z* 509 (1, M^+), 480 (0.4, $M^+ - C_2H_5$), 439 (15, $M^+ - C_2H_5 - CNMe$). IR (CH_2Cl_2): ν(CN) 2148 cm^{-1}. ^{1}H-NMR (C_6D_6, 90 MHz): δ 4.46 (s, 3H, C_6H_3 of mes), 3.17, 2.18 (both m, 1H each, $OsCH_2$), 2.65 (s, 3H, CNMe), 2.00 (s, 9H, C_6Me_3 of mes), 1.83 (dd, *J*(HH) = 7.6 Hz, 3H, CH_2CH_3).

*3.8. Preparation of [(mes)OsHBr(CNXyl)] (**28**)*

A suspension of 120 mg (0.23 mmol) of **5** in 8 ml of benzene was treated at 5°C with 2.3 ml of a 0.25 M solution (0.58 mmol) of $C_6H_{11}MgBr$ in ether. After warming to r.t., the reaction mixture was worked up analogously as described for **26**. With benzene, a yellow fraction was eluted from which after removal of the solvent a yellow solid was isolated; yield 84 mg (70%), m.p. 146°C (dec.). Anal. Found: C, 41.09; H, 4.40; N, 2.60. Calc. for $C_{18}H_{22}BrNOs$: C, 41.38; H, 4.24; N, 2.68%. MS (70 eV): *m*/*z* 523 (1, M^+), 522 (1, $M^+ - H$), 391 (2, $M^+ - H - CNXyl$). IR (CH_2Cl_2): ν(CN), ν(OsH) 2089, 2020 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 6.73 (s, 3H, C_6H_3 of Xyl), 4.63 (s, 3H, C_6H_3 of mes), 2.35 (s, 6H, C_6Me_2 of Xyl), 2.11 (s, 9H, C_6Me_3 of mes), −8.78 (s, 1H, OsH).

*3.9. Preparation of [(mes)Os(CH_3)$_2$(CNR)] (**29**–**32**)*

A suspension of 0.25 mmol of **1**, **2**, **4** or **5** in 10 ml of benzene was treated at 5°C with 0.55 ml of a 0.9 M solution (0.50 mmol) of MeLi/LiCl in ether. After the reaction mixture was warmed to r.t., it was stirred for 2.5 h and then ca. 100 mg of basic Al_2O_3 was added. The solvent was removed in vacuo, the residue was extracted with 2 ml of benzene and the extract was chromatographed on Al_2O_3 (basic, activity grade III, height of column 4 cm). With hexane, a yellow fraction was eluted from which, after the solvent was evaporated, a yellow solid was isolated.

29: Yield 74 mg (79%). ^{13}C-NMR (C_6D_6, 100.6 MHz): δ 152.4 (s, *C*NMe), 99.0 (s, CH of mes), 77.8 (s, *C*CH_3 of mes), 28.5 (s, CH_3 of CNMe), 18.5 (s, CH_3 of mes), −21.7 (s, $OsCH_3$). Other spectroscopic and analytical data were already reported [6].

30: Yield 57 mg (54%), m.p. 46°C (dec.). Anal. Found: C, 45.84; H, 6.65; N, 3.26. Calc. for $C_{16}H_{27}NOs$: C, 45.37; H, 6.42; N, 3.31%. MS (70 eV): *m*/*z* 425 (19, M^+), 410 (10, $M^+ - CH_3$), 327 (5, $M^+ - CH_3 - CN\textit{t}Bu$), 312 (1, (mes)$Os^+$). IR ($CH_2Cl_2$): ν(CN) 2100, 2045 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 4.36 (s, 3H, C_6H_3 of mes), 1.97 (s, 9H, C_6Me_3 of mes), 1.17 (s, 9H, *t*Bu), 0.86 (s, 6H, $OsCH_3$).

31: Yield 84 mg (75%), m.p. 23°C (dec.). Anal. Found: C, 47.99; H, 6.31; N, 3.20. Calc. for $C_{18}H_{29}NOs$: C, 48.08; H, 6.50; N, 3.12%. MS (70 eV): *m*/*z* 451 (42, M^+), 436 (69, $M^+ - CH_3$), 338 (100, (mes)OsCN$^+$), 327 (7, M$^+$ − CH$_3$ − CN*t*Bu), 312 (3, (mes)Os$^+$). IR (CH$_2$Cl$_2$): ν(CN) 2081, 2051 cm^{-1}. ^{1}H-NMR (C$_6$D$_6$, 400 MHz): δ 4.39 (s, 3H, C$_6$H$_3$ of mes), 3.38 (m, 1H, CH of C$_6$H$_{11}$), 2.00 (s, 9H, C$_6$Me$_3$ of mes), 1.56 (m, 4H, C$_6$H$_{11}$), 1.43, 1.08, 0.99 (all m, 2H each, C$_6$H$_{11}$).

32: Yield 91 mg (77%), m.p. 122°C (dec.). Anal. Found: C, 50.89; H, 5.89; N, 2.98. Calc. for C$_{20}$H$_{27}$NOs: C, 50.93; H, 5.77; N, 2.97%. MS (70 eV): *m*/*z* 473 (43, M$^+$), 458 (54, M$^+$ − CH$_3$), 327 (5, M$^+$ − CH$_3$ − CNXyl), 312 (1, (mes)Os$^+$). IR (CH$_2$Cl$_2$): ν(CN) 2048, 2015 cm^{-1}. ^{1}H-NMR (C$_6$D$_6$, 400 MHz): δ 6.80 (s, 3H, C$_6$H$_3$ of Xyl), 4.41 (s, 3H, C$_6$H$_3$ of mes), 2.33 (s, 6H, C$_6$Me$_2$ of Xyl), 1.95 (s, 9H, C$_6$Me$_3$ of mes), 0.93 (s, 6H, OsCH$_3$). ^{13}C-NMR (C$_6$D$_6$, 100.6 MHz): δ 162.2 (s, *C*NXyl), 133.7, 132.0, 127.8, 125.0 (all s, ring-C of Xyl), 101.3 (s, *C*CH$_3$ of mes), 80.0 (s, CH of mes), 19.4 (s, CH$_3$ of Xyl), 18.6 (s, CH$_3$ of mes), −20.5 (s, OsCH$_3$).

3.10. Reaction of compounds *1*, *2*, *4* and *5* with MeLi/LiI

A suspension of 0.25 mmol of **1**, **2**, **4** or **5** in 10 ml of benzene was treated at 5°C with 0.35 ml of a 1.5 M solution (0.53 mmol) of MeLi/LiI in ether. After the reaction mixture was warmed to r.t., it was worked up analogously as described for **29**–**32**. By chromatography on Al$_2$O$_3$ two fractions were eluted: with 3:1 hexane–benzene a yellow fraction and with 2:1 benzene–dichloromethane an orange fraction. From the first, a yellow solid consisting of **29**, **30**, **31** or **32** was obtained; yield 40–55%. The orange fraction gave after removal of the solvent an orange–yellow solid consisting of **26**, **33**, **34** or **35**. For **26**, the yield was 37 mg (30%). For analytical and spectroscopic data of **26** see Ref. [6].

33: Yield 56 mg (42%), m.p. 111°C (dec.). Anal. Found: C, 33.79; H, 4.63; N, 2.91. Calc. for C$_{15}$H$_{24}$INOs: C, 33.65; H, 4.52; N, 2.62%. MS (70 eV): *m*/*z* 537 (44, M$^+$), 522 (28, M$^+$ − CH$_3$), 466 (100, M$^+$ − N*t*Bu), 439 (93, (mes)OsI$^+$). IR (CH$_2$Cl$_2$): ν(CN) 2119, 2081 cm^{-1}. ^{1}H-NMR (C$_6$D$_6$, 90 MHz): δ 4.44 (s, 3H, C$_6$H$_3$ of mes), 2.03 (s, 9H, C$_6$Me$_3$ of mes), 1.62 (s, 3H, OsCH$_3$), 1.15 (s, 9H, *t*Bu). ^{13}C-NMR (C$_6$D$_6$, 100.6 MHz): δ 138.1 (s, *C*N*t*Bu), 97.9 (s, *C*CH$_3$ of mes), 78.0 (s, CH of mes), 56.5 (s, *C*CH$_3$ of *t*-Bu), 31.6 (s, CH$_3$ of *t*Bu), 19.4 (s, CH$_3$ of mes), −24.3 (s, OsCH$_3$).

34: Yield 47 mg (34%), m.p. 70°C. Anal. Found: C, 36.38; H, 4.60; N, 2.54. Calc. for C$_{17}$H$_{26}$INOs: C, 36.36; H, 4.67; N, 2.49%. MS (70 eV): *m*/*z* 563 (42, M$^+$), 548 (55, M$^+$ − CH$_3$), 466 (100, M$^+$ − NCy), 439 (81, M$^+$ − CH$_3$ − CNCy), 436 (44, M$^+$ − I), 312 (1, (mes)Os$^+$). IR (CH$_2$Cl$_2$): ν(CN) 2125 cm^{-1}. ^{1}H-NMR (C$_6$D$_6$, 400 MHz): δ 4.46 (s, 3H, C$_6$H$_3$ of mes), 3.47 (m, 1H, CH of C$_6$H$_{11}$), 2.04 (s, 9H, C$_6$Me$_3$ of mes), 1.71 (s, 3H, OsCH$_3$), 1.63 (m, 2H, C$_6$H$_{11}$), 1.46 (m, 4H, C$_6$H$_{11}$), 1.06, 0.96 (both m, 2H each, C$_6$H$_{11}$). ^{13}C-NMR (C$_6$D$_6$, 100.6 MHz): δ 136.8 (s, *C*NCy), 97.7 (s, *C*CH$_3$ of mes), 78.0 (s, CH of mes), 54.0 (s, CH of C$_6$H$_{11}$), 34.1, 25.2, 23.0 (all s, CH$_2$ of C$_6$H$_{11}$), 19.4 (s, CH$_3$ of mes), −24.3 (s, OsCH$_3$).

35: Yield 47 mg (32%), m.p. 158°C (dec.). Anal. Found: C, 39.56; H, 4.37; N, 2.43. Calc. for C$_{19}$H$_{24}$INOs: C, 39.11; H, 4.15; N, 2.40%. MS (70 eV): *m*/*z* 585 (37, M$^+$), 570 (100, M$^+$ − CH$_3$), 439 (81, M$^+$ − CH$_3$ − CNXyl). IR (CH$_2$Cl$_2$): ν(CN) 2082, 2017 cm^{-1}. ^{1}H-NMR (C$_6$D$_6$, 400 MHz): δ 6.75 (m, 3H, C$_6$H$_3$ of Xyl), 4.48 (s, 3H, C$_6$H$_3$ of mes), 2.37 (s, 6H, C$_6$Me$_2$ of Xyl), 2.02 (s, 9H, C$_6$Me$_3$ of mes), 1.74 (s, 3H, OsCH$_3$). ^{13}C-NMR (C$_6$D$_6$, 100.6 MHz): δ 147.9 (s, *C*NXyl), 135.1, 129.9, 127.9, 126.8 (all s, ring-C of Xyl), 99.4 (s, *C*CH$_3$ of mes), 80.1 (s, CH of mes), 19.6 (s, CH$_3$ of Xyl), 19.5 (s, CH$_3$ of mes), −24.0 (s, OsCH$_3$).

3.11. Preparation of [(mes)Os(CH$_3$)Cl(CNXyl)] (*36*)

A slow stream of dry HCl was passed through a solution of 71 mg (0.15 mmol) of **32** in 5 ml of CH$_2$Cl$_2$ for 30 s at −78°C. The solvent was removed, the residue was dissolved in 2 ml of benzene and the solution was chromatographed on Al$_2$O$_3$ (basic, activity grade III, height of column 4 cm). With 1:3 C$_6$H$_6$–CH$_2$Cl$_2$ a yellow fraction, and with CH$_2$Cl$_2$ an orange fraction were eluted. From the latter, the dichloro complex **5** (49 mg, 64%) was isolated. The yellow fraction afforded after evaporation of the solvent compound **36** as a yellow solid; yield 20 mg (27%), m.p. 146°C (dec.). Anal. Found: C, 46.66; H, 4.84; N, 2.86. Calc. for C$_{19}$H$_{24}$ClNOs: C, 46.38; H, 4.92; N, 2.85%. MS (70 eV): *m*/*z* 493 (10, M$^+$), 478 (51, M$^+$ − CH$_3$), 347 (49, M$^+$ − CH$_3$ − CNXyl). IR (CH$_2$Cl$_2$): ν(CN) 2089 cm^{-1}. ^{1}H-NMR (C$_6$D$_6$, 400 MHz): δ 6.74 (m, 3H, C$_6$H$_3$ of Xyl), 4.45 (s, 3H, C$_6$H$_3$ of mes), 2.33 (s, 6H, C$_6$Me$_2$ of Xyl), 1.94 (s, 9H, C$_6$Me$_3$ of mes), 1.60 (s, 3H, OsCH$_3$).

3.12. Preparation of [(mes)Os{=C(CH$_3$)NHC$_6$H$_4$}I] (*37*)

A suspension of 130 mg (0.27 mmol) of **3** in 10 ml of benzene was treated with 0.4 ml of a 1.5 M solution (0.60 mmol) of MeLi/LiI in ether. After the reaction mixture was warmed to r.t., it was worked up analogously as described for **29**–**32**. Column chromatography on Al$_2$O$_3$ (basic, activity grade III) with benzene afforded a red fraction from which after removal of the solvent an orange–red solid was obtained; yield 66 mg (44%), m.p. 160°C (dec.). Anal. Found: C, 36.52; H, 3.50; N, 2.46. Calc. for C$_{17}$H$_{20}$INOs: C, 36.76; H, 3.63; N, 2.52%. MS (70 eV): *m*/*z* 557 (85, M$^+$), 439

(3, $M^+ - CH_3 - CNPh$), 430 (34, $M^+ - I$). IR (CH_2Cl_2): ν(NH) 3358 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 10.0 (br s, 1H, NH), 7.73, 7.01, 6.71 (all m, 4H, C_6H_4), 4.95 (s, 3H, C_6H_3 of mes), 3.09 (s, 3H, $=CCH_3$), 2.20 (s, 9H, C_6Me_3 of mes). ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ 230.0 (s, Os=C), 152.0, 151.2, 140.4, 123.7, 121.5 (all s, ring-C of C_6H_4), 94.3 (s, CCH_3 of mes), 81.5 (s, CH of mes), 37.9 (s, $=CCH_3$), 19.8 (s, CH_3 of mes).

3.13. Preparation of [(mes)Os(C_2H_4)(CNMe)] (**38**)

A solution of 85 mg (0.22 mmol) of **29** in 4 ml of ether was treated dropwise at −78°C with a solution of 82 mg (0.21 mmol) of $[CPh_3]PF_6$ in 3 ml of CH_2Cl_2. After the reaction mixture was warmed to r.t., it was stirred for 30 min and then concentrated to ca. 3 ml in vacuo. Addition of 10 ml of ether led to the formation of a brown oily precipitate, which was separated from the mother liquor and washed three times with 5 ml of ether. The oily residue was dissolved in 7 ml of THF and under vigorous stirring the solution was treated with an excess (ca. 150 mg) of NaH. After the reaction mixture was stirred for 90 min, the solvent was removed and the residue was extracted three times with 10 ml of benzene. The combined extracts were filtered, the filtrate was evaporated in vacuo and the crude product was recrystallized from hexane at −78°C. A pale yellow solid was obtained; yield 27 mg (33%), m.p. 75°C (dec.). Anal. Found: C, 41.44; H, 5.08; N, 3.88. Calc. for $C_{13}H_{19}NOs$: C, 41.14; H, 5.05; N, 3.69%. MS (70 eV): m/z 381 (9, M^+), 353 (15, $M^+ - C_2H_4$). IR (hexane): ν(CN) 1920 cm^{-1}. ^{1}H-NMR (C_6D_6, 90 MHz): δ 4.68 (s, 3H, C_6H_3 of mes), 2.71 (s, 3H, CNMe), 2.19 (m, 2H, C_2H_4), 2.10 (s, 9H, C_6Me_3 of mes), 1.72 (m, 2H, C_2H_4).

3.14. Preparation of [(mes)OsH(C_2H_4)(CNMe)]BF_4 (**39**)

A solution of 30 mg (0.08 mmol) of **38** in 5 ml of ether was treated at −78°C with a solution of HBF_4 in ether until the yellow color disappeared. A yellow–brown solid precipitated which was separated from the mother liquor, washed 5 times with 5 ml of ether and dried; yield 32 mg (86%). IR (CH_2Cl_2): ν(CN), ν(OsH) 2200 cm^{-1}. ^{1}H-NMR (CD_2Cl_2, 90 MHz): δ 5.99 (s, 3H, C_6H_3 of mes), 3.54 (s, 3H, CNMe), 2.61 (m, 2H, C_2H_4), 2.44 (s, 9H, C_6Me_3 of mes), 2.23 (m, 2H, C_2H_4), −12.54 (s, 1H, OsH).

3.15. Photolysis of compound **38** in benzene

A solution of 15 mg (0.04 mmol) of **38** in 1 ml of benzene was irradiated at 5°C in an NMR tube with a 500 W UV lamp (Osram HBO) for 2 h. After the UV irradiation was stopped, the ^{1}H-NMR spectrum of the solution displayed besides the signals of **38** (ca. 25%) and free mesitylene (ca. 10%) those of the hydrido complex **19**; yield ca. 65%.

3.16. Low-temperature photolysis of compound **38** in toluene-d_8

A solution of 15 mg (0.04 mmol) of **38** in 0.5 ml of toluene-d_8 was irradiated at −80°C in an NMR tube with a 500 W UV lamp (Osram HBO) for 3 h. After the UV irradiation was stopped, the ^{1}H-NMR spectrum of the solution displayed besides the signals of free mesitylene those of compound **40**; yield ca 35%. ^{1}H-NMR (toluene-d_8, 90 MHz): δ 8.40 (ddd, J(HH) = 18.0, 11.0, 1.5 Hz, 1H, OsCH=CH_2), 6.85 (dd, J(HH) = 11.0, 4.8 Hz, 1H, one H of =CH_2 *cis* to OsCH), 5.83 (dd, J(HH) = 18.0, 4.8 Hz, 1H, one H of =CH_2 *trans* to OsCH), 4.63 (s, 3H, C_6H_3 of mes), 2.70 (s, 3H, CNMe), 2.14 (s, 9H, C_6Me_3 of mes), −9.71 (br s, 1H, OsH).

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