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Chemical behaviour of alkyl imido cyclopentadienyl niobium and tantalum(V) complexes in insertion processes. X-ray crystal structures of [MCpCl(NAr){η^2-C(Me)=NAr}] (Ar = 2,6-$Me_2C_6H_3$; M = Nb, Cp=η^5-$C_5H_4SiMe_3$; M = Ta, Cp = η^5-C_5Me_5) and [Ta(η^5-C_5Me_5)Me(NAr){η^2-C(CH_2CMe_2Ph)=O}] (Ar = 2,6-$Me_2C_6H_3$)

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Abstract

Pure imido η^2-iminoacyl derivatives [MCpX(NAr){η^2-C(R)=NAr}] (Ar = 2,6-$Me_2C_6H_3$; M = Nb, Cp = η^5-$C_5H_4SiMe_3$ = Cp′, X = Cl, R = Me, **1**; X = Me, R = NMe_2, **2**; Me, **3**; X = R = CH_2SiMe_3, **4**; CH_2CMe_3, **5**; CH_2Ph, **6**; M = Ta, Cp = η^5-C_5Me_5 = Cp*, X = Cl, R = Me, **7**; CH_2SiMe_3, **8**; CH_2CMe_2Ph, **9**; CH_2CMe_3, **10**; $CH_2C_6H_5$, **11**; 2-(CH_2NMe_2)C_6H_4, **12**; NMe_2, **13**; X = R = CH_2SiMe_3, **14**; CH_2CMe_2Ph, **15**; CH_2CMe_3, **16**; $CH_2C_6H_5$, **17**; C_6H_5, **18**) can be prepared by reaction of chloro alkyl or dialkyl imido complexes MCpXR(NAr) with 1 equivalent of 2,6-$Me_2C_6H_3NC$. Reaction of alkyl methyl imido complexes TaCp*RMe(NAr) with 1 equivalent of isocyanide 2,6-$Me_2C_6H_3NC$ takes place with migration of alkyl or methyl group, leading to the formation of a mixture of methyl η^2-alkyliminoacyl [TaCp*Me(NAr){η^2-C(R)=NAr}] (Ar = 2,6-$Me_2C_6H_3$; R = CH_2SiMe_3, **19**; CH_2Ph, **21**; CH_2CMe_2Ph, **23**; CH_2CMe_3, **25**; C_6H_5, **27**; 2-(CH_2NMe_2)C_6H_4, **29**; NMe_2, **30**) and alkyl η^2-methyliminoacyl [TaCp*R(NAr){η^2-C(Me)=NAr}] (Ar = 2,6-$Me_2C_6H_3$; R = CH_2SiMe_3, **20**; CH_2Ph, **22**; CH_2CMe_2Ph, **24**; CH_2CMe_3, **26**; C_6H_5, **28**) complexes. Alkyl imido derivatives also react with CO to give alkyl η^2-acyl [TaCp*X(NAr){η^2-C(R)=O}] (Ar = 2,6-$Me_2C_6H_3$; X = R = CH_2SiMe_3, **31**; CH_2CMe_2Ph, **32**; CH_2CMe_3, **33**; CH_2Ph, **34**), chloro η^2-acyl (X = Cl, R = CH_2CMe_2Ph, **35**; NMe_2, **36**) and methyl η^2-acyl (X = Me, R = CH_2CMe_2Ph, **37**; CH_2CMe_3, **38**) complexes. Dinuclear ene diolate complexes [{TaCp*X(NAr)}$_2${μ-η^2-OC(R)=C(R)O}] (Ar = 2,6-$Me_2C_6H_3$; X = Cl, R = CH_2CMe_3, **39**; X = Me, R = 2-(CH_2NMe_2)C_6H_4, **40**) are formed by reaction of the chloro and methyl alkyl imido derivatives with carbon monoxide, whereas using [TaCp*XR(NAr)] (Ar = 2,6-$Me_2C_6H_3$; X = Cl, R = CH_2CMe_3; X = R = Ph) a different sequence of reactions takes place leading finally to oxo η^2-iminoacyl complexes [TaCp*X(O){η^2-C(R)=NAr}] (X = Cl, R = CH_2CMe_3, **41**; X = R = Ph, **42**). All compounds were characterised by NMR (^{1}H, ^{13}C) spectroscopy and IR measurements. The molecular structures of **1**, **7** and **37** were studied by X-ray diffraction methods and are discussed. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Niobium; Tantalum; Imido η^2-iminoacyl, η^2-acyl cyclopentadienyl complexes

1. Introduction

Transfer of alkyl groups from transition metals to coordinated unsaturated molecules [1], such as carbon monoxide and isocyanides, is an important organometallic reaction that has deservedly received relevant synthetic, mechanistic and theoretical studies [2]. The resulting metal-η^2-acyl and metal-η^2-iminoacyl derivatives are key and versatile reactive intermediates in many transition-metal-promoted stoichiometric and catalytic organometallic transformations [3].

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In the last few years, we have realized extensive research efforts on transition-metal complexes with multiply bonded ligands, basically high-valent niobium and tantalum complexes containing cyclopentadienyl ligands and strong π-donor organoimido substituents [4]. Further, we have recently reported [5] the reactions of chloro methyl tantalum(V) complexes with carbon monoxide and isocyanides. Following our recent work, we report herein a systematic study of the insertion and intramolecular rearrangement processes observed when 2,6-$Me_2C_6H_3NC$ and CO react with alkyl chloro, dialkyl and mixed alkyl derivatives of imido cyclopentadienyl niobium and tantalum(V). All compounds were fully characterized and further, some of them were studied by X-ray diffraction methods.

2. Results and discussion

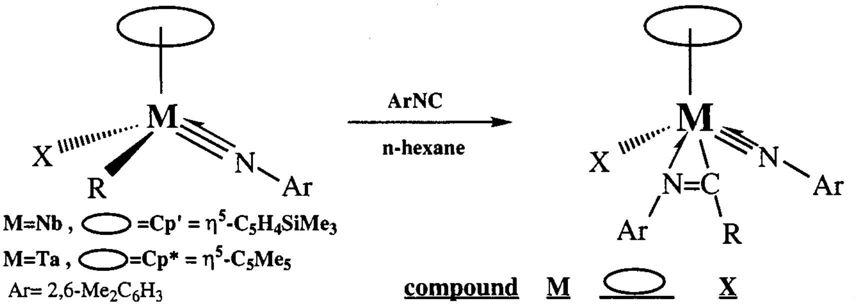
2.1. Reactions with isocyanides

When 2,6-$Me_2C_6H_3NC$ is added to *n*-hexane solutions of the chloro alkyl or dialkyl imido complexes [MCpXR(NAr)] (Ar = 2,6-$Me_2C_6H_3$; M = Nb, Cp = Cp′; M = Ta, Cp = Cp*) an insertion reaction takes place to give the stable 18-electron imido η^2-iminoacyl derivatives [MCpX(NAr){η^2-C(R)=NAr}] (Ar = 2,6-$Me_2C_6H_3$; M = Nb, Cp = Cp′, X = Cl, R = Me, **1**; X = Me, R = NMe_2, **2**; Me, **3**; X = R = CH_2SiMe_3, **4**; CH_2CMe_3, **5**; CH_2Ph, **6**; M = Ta, Cp = Cp*, X = Cl, R = Me, **7**; CH_2SiMe_3, **8**; CH_2CMe_2Ph, **9**; CH_2CMe_3, **10**; $CH_2C_6H_5$, **11**; 2-(CH_2NMe_2)C_6H_4, **12**; NMe_2, **13**; X = R = CH_2SiMe_3, **14**; CH_2CMe_2Ph, **15**; CH_2CMe_3, **16**; $CH_2C_6H_5$, **17**; C_6H_5, **18**) (Scheme 1). The complex **7** was described by us before [5] and in this paper we only discuss its study by X-ray diffraction.

In the case of dialkyl derivatives (X = R = alkyl) the migration of the second alkyl group observed for $TaCp^*Cl_2Me_2$ [4a] does not take place and the presence of an excess of isocyanide does not produce a second insertion reaction in the M-C(alkyl) or M-C(iminoacyl) bonds [1f,3d,i,j].

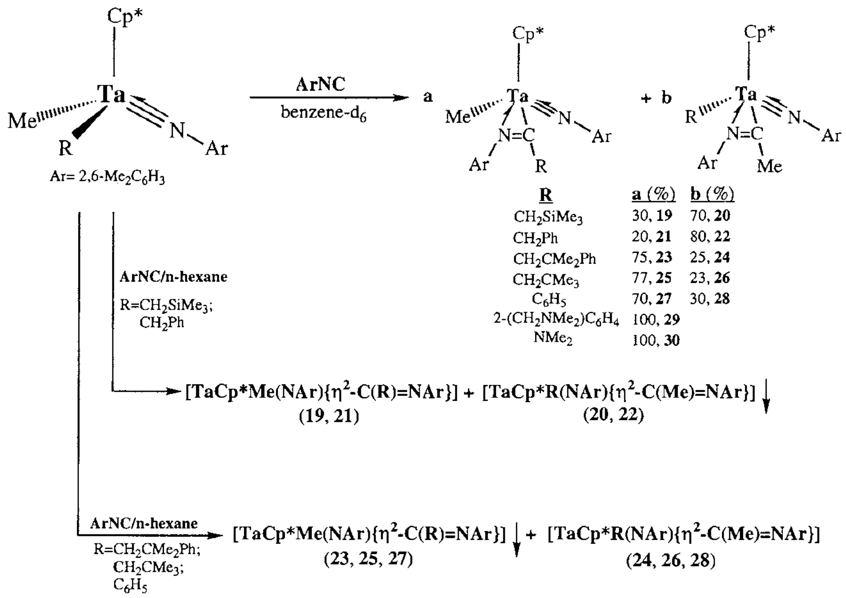
The addition of one equivalent of 2,6-$Me_2C_6H_3NC$ to benzene-d_6 solutions of the alkyl methyl imido complexes under rigorously anhydrous conditions (sealed NMR tube with hydrophobic internal surface) gives a mixture of methyl η^2-alkyliminoacyl [TaCp*Me(NAr)-{η^2-C(R)=NAr}] (Ar = 2,6-$Me_2C_6H_3$; R = CH_2SiMe_3, **19**; CH_2Ph, **21**; CH_2CMe_2Ph, **23**; CH_2CMe_3, **25**; C_6H_5, **27**; 2-(CH_2NMe_2)C_6H_4, **29**; NMe_2, **30**) and alkyl η^2-methyliminoacyl [TaCp*R(NAr){η^2-C(Me)=NAr}] (Ar = 2,6-$Me_2C_6H_3$; R = CH_2SiMe_3, **20**; CH_2Ph, **22**; CH_2CMe_2Ph, **24**; CH_2CMe_3, **26**; C_6H_5, **28**) complexes in ratios determined from ^{1}H-NMR spectra and shown in Scheme 2.

When the same reaction is repeated at room temperature (r.t.) by using *n*-hexane as solvent in a dry box, alkyl η^2-methyliminoacyl (R = CH_2SiMe_3, **20**;



compound	M	⬭	X	R
1	Nb	Cp'	Cl	Me
2			Me	NMe_2
3			Me	Me
4			CH_2SiMe_3	CH_2SiMe_3
5			CH_2CMe_3	CH_2CMe_3
6			CH_2Ph	CH_2Ph
7	Ta	Cp*	Cl	Me
8				CH_2SiMe_3
9				CH_2CMe_2Ph
10				CH_2CMe_3
11				CH_2Ph
12				2-(CH_2NMe_2)C_6H_4
13				NMe_2
14			CH_2SiMe_3	CH_2SiMe_3
15			CH_2CMe_2Ph	CH_2CMe_2Ph
16			CH_2CMe_3	CH_2CMe_3
17			CH_2Ph	CH_2Ph
18			Ph	Ph

Scheme 1.



Scheme 2.

CH$_2$Ph, **22**) and methyl η^2-alkyliminoacyl (R = CH$_2$CMe$_2$Ph, **23**; CH$_2$CMe$_3$, **25**; C$_6$H$_5$, **27**) complexes, major components in the already mentioned mixture, are isolated as insoluble microcrystalline solids. Further, when the resulting suspension of the above experiment is evaporated to dryness, a ^{1}H-NMR spectrum in benzene-d_6 of the crude residue gave the same result. Yields reflect the relative case of migration [6] of a wide variety of alkyl groups, such as 2-(CH$_2$NMe$_2$)C$_6$H$_4$ $\approx$ NMe$_2$ > CH$_2$CMe$_2$Ph $\approx$ CH$_2$C-Me$_3$ > C$_6$H$_5$ > *Me* > CH$_2$SiMe$_3$ > CH$_2$Ph as compared with methyl group. Our particular contribution also establishes the regioselective migration of the 2-[(dimethylamino)methyl)]-phenyl and dimethylamido groups. The preferential migration of the NMe$_2$ moiety, in the case of the starting amido methyl niobium and tantalum derivatives to give methyl η^2-iminocarbamoyl complexes **2** and **30**, is quite unusual because in similar amido alkyl or methyl titanium [7], zirconium [8], tungsten [9] and uranium [10] complexes the insertion occurs preferentially at the metal–carbon (alkyl) bond.

Exactly the same η^2-iminoacyl complexes **19**–**30** are obtained by reaction of 2 equivalents of the isocyanide with the starting mixed alkyl imido derivatives in benzene-d_6 solutions at r.t. The bis-(η^2-iminoacyl) derivatives cannot be detected by ^{1}H-NMR spectroscopy.

All of the complexes **1**–**30** are soluble in aromatic, chlorinated and ethereal solvents; further the complexes **2**–**5**, **19**, **21**, **23**, **24**, **26** and **28** are soluble in saturated hydrocarbons whereas the remaining complexes are only slight soluble.

The IR spectra (Table 1) of all complexes show the characteristic absorptions for the pentamethylcyclopentadienyl ($\nu_{C-C} \approx 1026$ cm^{-1}) [11], trimethylsilylcyclopentadienyl ($\nu_{C-H} \approx 838$ cm^{-1}) [12] rings and for the trimethylsilyl substituent (δ_{as} CH$_3 \approx 1249$ cm^{-1}) [12d, 13]. Absorptions due to the C(R)=N, M=N, M–C and M–Cl stretching vibrations are observed at $\approx$1633(Nb), 1614(Ta) [14], 1305(Nb), 1322(Ta) [15], 631(Nb), 697(Ta) [16] and 356(Nb), 355(Ta) [12d, 17] cm^{-1}, respectively.

The ^{1}H- and ^{13}C{^{1}H}-NMR data (Table 2) of the η^2-iminoacyl complexes **1**–**30** is in agreement with the expected pseudo-square-pyramidal geometry found for similar chiral niobium and tantalum derivatives [5]. The ^{1}H-NMR spectra show AB spin systems for diastereotopic α-CH$_2$ protons of alkyl groups in the complexes **4**–**6**, **8**–**12**, **14**–**17**, **20**, **22**–**26** and **29**, the expected two resonances for the inequivalent methyl substituents of the β-CMe$_2$ groups in the ^{1}H- and ^{13}C{^{1}H}-NMR spectra of **9**, **15**, **23** and **24** and four proton and five carbon resonances for the trimethylsilylcyclopentadienyl ring in the complexes **16** due to the chiral character of the metal atoms. The observation of two inequivalent methyl groups for the 2,6-Me$_2$C$_6$H$_3$ moiety of the η^2-iminoacyl ligand in the complexes **1**–**6**, **8**–**13**, **15**–**18**, **20**, **22**, **23**, **25**, **27** and **30** is consistent with the restricted rotation of the aryl group around the N–C$_i$(aryl) bond, whereas the detection of broad signals for *ortho*-methyl(phenyl) groups of the imido ligand in the complexes **8**–**11**, **1**–**17**, **20**, **22**, **23**, **25**, **27** and **30** is due to a slow (on the NMR time scale) rotation around the N$_{imido}$-C$_i$(aryl) bond.

The η^2-iminoacyl carbon signals appear at $\delta \approx 230$ and 243 for niobium and tantalum derivatives, respec-

Table 1
IR [a] data of the new complexes

	$\nu_{\mathrm{C(R)=N}}$	$\nu_{\mathrm{C(R)=O}}$	$\nu_{\mathrm{M=N}}$	$\nu_{\mathrm{C-C}}$(Cp*)	$\nu_{\mathrm{M-C}}$	$\nu_{\mathrm{M-Cl}}$	Others
1	1655(m)		1307(m)				1247(m)[$\nu_{\delta s}(\mathrm{Me_3Si})$], 1170(w), 1092(m), 1043(w), 902(w), 839(m), [$\nu_{\mathrm{C-H}}(\mathrm{Cp'})$], 630(w)
2	1636(s)		1313(s)		629(w)		1462(vs), 1245(s)[$\nu_{\delta s}(\mathrm{Me_3Si})$],1168(m), 1080(m), 1044(m), 905(m), 834(vs) [$\nu_{\mathrm{C-H}}(\mathrm{Cp'})$], 670(w), 474(w)
3	1639(m)		1312(s)		633(w)		1243(m)[$\nu_{\delta s}(\mathrm{Me_3Si})$], 1188(m), 1094(m), 1043(m), 906(m), 838(vs)[$\nu_{\mathrm{C-H}}(\mathrm{Cp'})$], 460(w)
4	1613(m)		1300(vs)		631(w)		1410(s), 1247(vs)[$\nu_{\delta s}(\mathrm{Me_3Si})$],1180(s), 1096(m), 1043(m), 905(m),840(s)[$\nu_{\mathrm{C-H}}(\mathrm{Cp'})$], 674(w)
5	1635(m)		1307(m)		632(w)		1410(s), 1247(m)[$\nu_{\delta s}(\mathrm{Me_3Si})$], 1180(m), 1094(m), 1044(m), 906(m), 840(s)[$\nu_{\mathrm{C-H}}(\mathrm{Cp'})$], 698(w)
6	1621(m)		1296(m)		632(w)		1461(vs),1247(m)[$\nu_{\delta s}(\mathrm{Me_3Si})$], 1177(m), 1094(m), 1031(m), 904(m),836(s)[$\nu_{\mathrm{C-H}}(\mathrm{Cp'})$], 698(m)
8	1585(m)		1318(m)	1023(m)		351(w)	1254(s)[$\nu_{\delta s}(\mathrm{Me_3Si})$], 1188(m), 1098(m), 843(m), 673(m), 221(w)
9	1655(vs)		1329(vs)	1027(m)		360(w)	1589(s), 1414(s), 1176(s), 1095(s), 983(m), 934(m), 919(m), 815(m), 757(vs), 741(m), 722(m), 699(m), 575(w), 548(w), 508(w), 300(m), 275(w), 217(w)
10	1603(m)		1310(vs)	1024(m)		351(w)	1585(m), 1094(m), 974(m), 836(w), 764(m), 392(w), 300(w), 221(w)
11	1619(s)		1322(vs)	1027(m)		357(m)	1589(s), 1588(m), 1180(m), 1093(s), 979(m), 918(m), 833(m),756(s), 702(m), 509(w), 469(w), 392(w), 298(m), 268(w)
12	1603(vs)		1312(vs)	1025(m)		358(w)	1580(m), 1212(m), 1151(w) 923(m), 859(w), 803(w), 764(m), 722(m), 394(w), 244(w), 217(w)
13	1611(vs)		1330(vs)	1027(m)			1587(m), 1261(m), 1183(w), 1095(s), 803(m), 783(m), 758(w), 722(w)
14	1574(s)		1330(vs)	1025(m)	539(w)		1252(s)[$\nu_{\delta s}(\mathrm{Me_3Si})$], 1148(w), 1096(s), 967(m), 947(m), 846(vs), 755(vs), 732(vs), 673(m), 462(w), 346(m), 266(w), 235(w), 221(w)
15	1644(m)		1321(s)	1028(m)	570(w)		1591(m), 1415(m), 1179(m), 1095(m), 976(m), 758(m), 698(m), 344(m), 240(w)
16	1580(s)		1315(vs)	1025(m)			1411(s), 1217(m), 1157(m), 1094(m), 969(m), 933(w), 808(w), 759(s), 727(s), 699(s), 619(w), 470(w), 390(w), 349(m), 292(w)
17	1621(m)		1321(vs)	1024(m)	573(w)		1590(m), 1201(m), 1171(m), 1094(m), 1056(m), 976(m), 826(m), 761(s), 739(vs), 697(s), 505(w), 469(w), 443(w), 391(w), 347(m), 256(w)
18	1580(s)		1315(vs)	1025(m)			1411(s), 1217(m), 1157(m), 1094(m), 969(m), 933(w), 808(w), 759(s), 727(s), 699(s), 619(w), 470(w), 390(w), 349(m), 292(w)
20	1613(s)		1330(vs)	1025(m)			1586(s), 1260(m)[$\nu_{\delta s}(\mathrm{Me_3Si})$], 1187(w), 1093(m), 978(m), 825(m), 764(vs), 689(m), 480(w), 347(m), 265(w), 226(w)
22	1614(s)		1331(vs)	1026(m)			1590(s), 1196(m), 1094(m), 979(m), 834(w), 761(s), 698(m), 352(m)
23	1589(s)		1320(s)	1025(m)			1183(m), 1095(m), 975(m), 757(s), 696(m), 477(w), 348(w)
25	1587(s)		1319(s)	1025(m)			1183(m), 1095(m), 974(w), 801(w), 761(m), 472(w), 392(w), 346(w), 274(w), 243(w)
27	1587(s)		1325(vs)	1027(m)			1228(m), 1160(m), 1094(m), 977(w), 810(w), 759(m), 693(m), 485(w), 347(m), 286(w)
29	1603(s)		1318(vs)	1031(m)			1580(s), 1210(m), 1152(m), 1094(m),976(m), 918(m), 858(w), 803(m), 762(vs), 721(m), 480(w), 351(m), 241(w)
30	1604(s)		1332(vs)	1029(m)	593(w)		1586(s), 1183(m), 1162(m), 1095(m), 1083(m), 983(w), 908(w), 784(m), 756(m), 722(w), 488(w)
31		1498(m)	1327(vs)	1037(m)			1587(m), 1249(s)[$\nu_{\delta s}(\mathrm{Me_3Si})$],1186(m), 1094(m), 948(s), 853(vs), 757(s), 671(m), 469(m), 354(m), 269(w)
32		1546(m)	1313(vs)	1028(s)	580(m)		1595(m), 1094(m), 976(w), 804(w), 760(vs), 700(vs), 348(m), 249(w)
33		1545(m)	1328(vs)	1024(m)			1587(m), 1095(m), 983(w), 759(vs), 723(s), 606(m), 414(m), 347(s), 258(w)
35		1547(m)	1330(vs)	1033(s)	550(m)		1586(w), 1279(m), 1094(m), 983(w), 768(vs), 722(w), 700(s), 366(m), 313(m), 233(m)
37		1545(m)	1333(vs)	1032(m)			1586(w), 1157(w), 1093(m), 980(w), 766(s), 700(m), 549(w), 484(m), 358(m)
38		1536(m)	1332(vs)	1023(m)			1586(w), 1156(w), 1093(s), 1052(m), 979(m), 757(s), 722(m), 627(w), 352(w), 222(w)
39			1330(vs)	1024(m)		366(m)	1588(w)[$\nu_{\mathrm{C=C}}$], 1537(m), 1162(w)[$\nu_{\mathrm{C=O}}$], 1094(m), 1053(m), 981(w), 909(m), 822(w)[$\nu_{\mathrm{Ta-O}}$], 762(vs), 723(s), 317(m), 215(w)
40			1334(vs)	1024(m)			1587(w)[$\nu_{\mathrm{C=C}}$], 1157(w)[$\nu_{\mathrm{C=O}}$], 1094(s), 981(m), 802(w)[$\nu_{\mathrm{Ta-O}}$], 761(vs), 648(w), 605(m), 510(s), 474(m), 346(s)
42	1601(s)			1026(m)			1236(m), 1158(m), 1090(m), 940(w), 901(vs)[$\nu_{\mathrm{Ta=O}}$], 809(w), 774(s), 726(s), 700(s), 352(m), 288(w), 250(w), 230(w)

[a] Nujol mull, ν in $\mathrm{cm^{-1}}$.

Table 2
^{1}H- and ^{13}C{^{1}H}-NMR data of the new complexes [a]

	^{1}H	^{13}C{^{1}H}
1	a, 6.90(m, 4H), 6.71[m, 2H, $H_3C_6Me_2N$, $H_3C_6Me_2N{=}C(Me)$], 6.26(m, 1H), 6.23 (m, 1H), 6.09(m, 1H), 5.62(m, 1H, $H_4C_5SiMe_3$), 2.49(s, 6H, $Me_2C_6H_3N$), 2.04[s, 3H, $(Me)C{=}NC_6H_3Me_2$], 1.92(s, 3H), 1.73[s, 3H, $Me_2C_6H_3N{=}C(Me)$], 0.30(s, 9H, $Me_3SiC_5H_4$)	a, 225.89[C (Me)=$NC_6H_3Me_2$], 155.38, 139.84[C_i, $C_6H_3Me_2N$, $C_6H_3Me_2N{=}C(Me)$],132.13, 126.67, 122.8[several phenyl, $C_6H_3Me_2N$,$C_6H_3Me_2N{=}C(Me)$], 117.6(C_i,$C_5H_4SiMe_3$),120.9, 112.7, 110.9,108.9 ($C_5H_4SiMe_3$), 21.85[$(Me)C{=}NC_6H_3Me_2$], 19.73 ($Me_2C_6H_3N$), 18.26, 18.15[$Me_2C_6H_3N{=}C(Me)$], -0.09($Me_3SiC_5H_4$)
2	a, 7.00(d, 2H, $^3J_{H-H} = 7.5$ Hz), 6.92(m, 1H), 6.87(t, 1H, $^3J_{H-H} = 7.5$ Hz), 6.82[m, 2H, $H_3C_6Me_2N$,$H_3C_6Me_2N{=}C(NMe_2)$], 6.72(m, 1H), 6.12(m, 1H), 6.02(m, 1H), 5.52(m, 1H, $H_4C_5SiMe_3$), 2.89[s, 3H, $^1J_{C-H} = 136.6$ Hz, $(Me_2N)C{=}NC_6H_3Me_2$], 2.50(s, 6H, $^1J_{C-H} = 124.9$ Hz, $Me_2C_6H_3N$), 2.18 [s, 3H, $^1J_{C-H} = 136.6$ Hz, $(Me_2N)C{=}NC_6H_3Me_2$], 1.86(s, 3H), 1.82[s, 3H, $Me_2C_6H_3N{=}C(NMe_2)$], 0.79(s, 3H, Me–Nb), 0.21(s, 9H, $Me_3SiC_5H_4$)	a, not observed[C $(NMe_2){=}NC_6H_3Me_2$], 142.82, 140[C_i,$C_6H_3Me_2N$,$C_6H_3Me_2N{=}C(NMe_2)$], 131.8, 127.5, 124.9, 120.6[several phenyl, $C_6H_3Me_2N$,$C_6H_3Me_2N{=}C(NMe_2)$], 114.2(C_i, $C_5H_4SiMe_3$), 117.74, 110.3, 108.8, 106.6($C_5H_4SiMe_3$), 44.54, 36.13[$(Me_2N)C{=}NC_6H_3Me_2$], 20.27($Me_2C_6H_3N$), 18.75, 18.36[$Me_2C_6H_3N{=}C(NMe_2)$], 13.00(br, Me–Nb), -0.20($Me_3SiC_5H_4$)
3	a, 6.93(d, 2H, $^3J_{H-H} = 7.5$ Hz), 6.87(m, 2H), 6.78(m, 1H), 6.68[t, 1H, $H_3C_6Me_2N$, $H_3C_6Me_2N{=}C(Me)$], 6.19(m, 1H), 5.99 (m, 1H), 5.73(m, 1H), 5.67(m, 1H, $H_4C_5SiMe_3$), 2.45(s, 6H, $Me_2C_6H_3N$), 2.15[s, 3H, $(Me)C{=}NC_6H_3Me_2$], 1.75(s, 3H), 1.59[s, 3H, $Me_2C_6H_3N{=}C(Me)$], 0.89(s, 3H, Me–Nb), 0.20(s, 9H, $Me_3SiC_5H_4$)	a, 229.1[$C(Me){=}NC_6H_3Me_2$], 155.61, 141.5[C_i, $C_6H_3Me_2N$,$C_6H_3Me_2N{=}C(Me)$], 131.3, 129.03, 126.5, 121.6[several phenyl, $C_6H_3Me_2N$, $C_6H_3Me_2N{=}C(Me)$], 113.1(C_i,$C_5H_4SiMe_3$), 115.6, 112.8, 109.6, 109.1($C_5H_4SiMe_3$), 22.66[$(Me)C{=}NC_6H_3Me_2$], 20.23($Me_2C_6H_3N$), 18.26, 18.17[$Me_2C_6H_3N{=}C(Me)$], 11.7(br, Me–Nb), 0.25($Me_3SiC_5H_4$)
4	a, 6.95(d, 2H), 6.86(m, 1H), 6.82(m, 1H), 6.77(m, 1H), 6.70[t, 1H, $^3J_{H-H} = 7.2$ Hz, $H_3C_6Me_2N$, $H_3C_6Me_2N{=}C(CH_2SiMe_3)$], 6.76(m, 1H), 6.27(m, 1H), 6.15(m, 1H), 5.50 (m, 1H, $H_4C_5SiMe_3$), 2.80, 2.07[AB, 2H, $^2J_{H-H} = 16.2$ Hz, $(H_2CSiMe_3)C{=}NC_6H_3Me_2$], 2.55(s, 6H, $Me_2C_6H_3N$), 2.12(s, 3H), 1.78[s, 3H, $Me_2C_6H_3N{=}C(CH_2SiMe_3)$], 0.93_{AV}(AB, 2H, $^2J_{H-H} = 12.3$ Hz, Nb–CH_2SiMe_3), 0.22(s, 9H, $Me_3SiC_5H_4$), 0.06(s, 9H, Me_3SiCH_2–Nb), -0.18[s, 9H, $(Me_3SiCH_2)C{=}NC_6H_3Me_2$]	a, 231.8[$C(CH_2SiMe_3){=}NC_6H_3Me_2$], 155.6, 143.7[$C_i$, $C_6H_3Me_2N$,$C_6H_3Me_2N{=}C(CH_2SiMe_3)$], 132.3, 131.75, 129.4, 125.64[several phenyl, $C_6H_3Me_2N$, $C_6H_3Me_2N{=}C(CH_2SiMe_3)$], 121.4, 117.5, 109.3, 109.1($C_5H_4SiMe_3$), 109.44(C_i, $C_5H_4SiMe_3$), 65.9(Nb–C H_2SiMe_3), 31.31[$(CH_2SiMe_3)C{=}NC_6H_3Me_2$], 20.6($Me_2C_6H_3N$), 18.75, 18.6[$Me_2C_6H_3N{=}C(CH_2SiMe_3)$], 3.64($Me_3SiC_5H_4$), 0.02($Me_3SiCH_2$–Nb), -0.02[$(Me_3SiCH_2)C{=}NC_6H_3Me_2$]
5	a, 7.07(m, 1H), 6.89(m, 4H), 6.69[t, 1H, $^3J_{H-H} = 7.2$ Hz, $H_3C_6Me_2N$, $H_3C_6Me_2N{=}C(CH_2CMe_3)$], 7.00(m, 1H), 6.31(m, 1H), 6.14(m, 1H), 5.50(m, 1H, $H_4C_5SiMe_3$), 2.62, 2.02[AB, $^2J_{H-H} = 12.6$ Hz $(Me_3CCH_2)C{=}NC_6H_3Me_2$], 2.58(s, 6H, $Me_2C_6H_3N$), 2.48, 0.87(AB, $^2J_{H-H} = 15$ Hz, Nb–CH_2CMe_3), 2.03(s, 3H), 1.65[s, 3H, $Me_2C_6H_3N{=}C(CH_2CMe_3)$], 1.12(s, 9H, Me_3CCH_2–Nb), 0.99[s, 9H, $(Me_3CCH_2)C{=}NC_6H_3Me_2$], 0.20(s, 9H, $Me_3SiC_5H_4$)	a, 232.8[$C(CH_2CMe_3){=}NC_6H_3Me_2$], 155.8, 144[$C_i$, $C_6H_3Me_2N$,$C_6H_3Me_2N{=}C(CH_2CMe_3)$], 131.5, 129.7, 128.8, 126.3, 121.7[several phenyl, $C_6H_3Me_2N$,$C_6H_3Me_2N{=}C(CH_2CMe_3)$], 113.4($C_i$, $C_5H_4SiMe_3$), 116.9, 110.13, 109.7, 108.6($C_5H_4SiMe_3$), 62(Nb–CH_2CMe_3), 51.2[$(CH_2CMe_3)C{=}NC_6H_3Me_2$], 46.9($Me_3CCH_2$–Nb), 35.7[$(Me_3CCH_2)C{=}NC_6H_3Me_2$], 35.5[$(Me_3CCH_2)C{=}NC_6H_3Me_2$], 30.45($Me_3CCH_2$–Nb), 21.3($Me_2C_6H_3N$), 18.6, 18.5[$Me_2C_6H_3N{=}C(CH_2CMe_3)$], 0.58($Me_3SiC_5H_4$)
6	a, 7.05(m, 3H), 6.94(m, 8H), 6.75[m, 5H, $H_3C_6Me_2N$, $H_3C_6Me_2N{=}C(CH_2C_6H_5)$, Nb–$CH_2C_6H_5$], 6.39(m, 1H), 5.93(m, 1H), 5.32(m, 1H), 5.20(m, 1H,$H_4C_5SiMe_3$), 3.72_{AV}[AB, 2H, $^2J_{H-H} = 14.8$ Hz, $(CH_2Ph)C{=}NC_6H_3Me_2$], 3.27_{AV}(AB, 2H, $^2J_{H-H}=10.2$ Hz, Nb–CH_2Ph), 2.48(s, 6H, $Me_2C_6H_3N$), 1.70(s, 3H), 1.45[s, 3H, $Me_2C_6H_3N{=}C(CH_2Ph)$], 0.13(s, 9H, $Me_3SiC_5H_4$).	a,230[$C(CH_2Ph) = NC_6H_3Me_2$], 155.42, 153.51, 141.8(C_i, $C_6H_3Me_2N$,$C_6H_3Me_2N{=}C(CH_2C_6H_5)$, Nb–$CH_2C_6H_5$], 132.2, 131, 130.1, 129, 126.4, 121.8, 121[several phenyl, $C_6H_3Me_2N$, $C_6H_3Me_2N{=}C(CH_2C_6H_5)$,Nb–$CH_2C_6H_5$], 115($C_i$, $C_5H_4SiMe_3$), 117.74, 113.1, 111.4, 108 ($C_5H_4SiMe_3$), 43.42[$(CH_2Ph)C{=}NC_6H_3Me_2$], 40.1(br, Nb–CH_2Ph), 20.5($Me_2C_6H_3N$), 18.4, 18[$Me_2C_6H_3N{=}C(CH_2Ph)$], -0.25($Me_3SiC_5H_4$)
8	b, 7.00(m, 3H, $H_3C_6Me_2N{=}C(CH_2SiMe_3)$], 6.86(d, 2H, $^3J_{H-H} = 7.5$ Hz), 6.55(t, 1H, $^3J_{H-H} = 7.5$ Hz, $H_3C_6Me_2N$), 2.90, 2.84 [AB, 2H, $^2J_{H-H} = 15$ Hz, $(H_2CSiMe_3)C{=}NC_6H_3Me_2$], 2.28(br, 6H, $Me_2C_6H_3N$), 2.05(s, 15H, C_5Me_5), 2.06(s, 3H), 1.90 [s, 3H, $Me_2C_6H_3N{=}C(CH_2SiMe_3)$], -0.07[s, 9H, $(Me_3SiCH_2)C{=}NC_6H_3Me_2$]	b, 259.90[$C(CH_2SiMe_3) = NC_6H_3Me_2$], 153.43–120.05[several phenyl, $C_6H_3Me_2N$, $C_6H_3Me_2N{=}C(CH_2SiMe_3)$], 115.55($C_5Me_5$), 29.56[$(CH_2CSiMe_3)C{=}NC_6H_3Me_2$], 19.70(br, $Me_2C_6H_3N$), 18.95, 18.68[$Me_2C_6H_3N{=}C(CH_2SiMe_3)$], 11.30($C_5Me_5$), 0.52[$(Me_3SiCH_2)C{=}NC_6H_3Me_2$]
9	b, 7.15(m, 2H), 6.96[m, 3H, $(H_5C_6Me_2CCH_2)C{=}NC_6H_3Me_2$], 7.15[m, 3H,$H_3C_6Me_2N{=}C(CH_2CMe_2Ph)$], 6.87 (d, 2H, $^3J_{H-H} = 7.3$ Hz), 6.57(t, 1H, $^3J_{H-H} = 7.3$ Hz, $H_3C_6Me_2N$), 3.50[q, 2H, $^2J_{H-H} = 14.65$ Hz, $(H_2CCMe_2Ph)C{=}NC_6H_3Me_2$], 2.30(br, 6H, $Me_2C_6H_3N$), 2.00(s, 15H, C_5Me_5), 1.86(s, 3H), 1.64[s, 3H, $Me_2C_6H_3N{=}C(CH_2CMe_2Ph)$], 1.51(s, 3H), 1.21[s, 3H, $(Me_2PhCCH_2)C{=}NC_6H_3Me_2$]	b, 238.31[$C(CH_2CMe_2Ph) = NC_6H_3Me_2$], 153.35–120.28[several phenyl, $C_6H_3Me_2N$, $C_6H_3Me_2N{=}C(CH_2CMe_2C_6H_5)$], 115.84($C_5Me_5$), 51.13[$(CH_2CMe_2Ph)C{=}NC_6H_3Me_2$], 38.94[$(CH_2CMe_2Ph)C{=}NC_6H_3Me_2$], 30.68, 29.36[$(CH_2CMe_2Ph)C{=}NC_6H_3Me_2$], 20.01($Me_2C_6H_3N$), 18.60, 18.53[$Me_2C_6H_3N{=}C(CH_2CMe_2Ph)$], 11.30($C_5Me_5$)

Table 2 (Continued)

	^1H	$^{13}C\{^1H\}$
10	b, 7.02[m, 3H, $H_3C_6Me_2N{=}C(CH_2CMe_3)$], 6.86(d, 2H, $^3J_{\mathrm{H-H}} = 7.5$ Hz), 6.57(t, 1H, $^3J_{\mathrm{H-H}} = 7.5$ Hz, $H_3C_6Me_2N$), 2.95[q, 2H, $^2J_{\mathrm{H-H}} = 13.18$ Hz, $(H_2CCMe_3)C{=}NC_6H_3Me_2$], 2.30(br, 6H, $Me_2C_6H_3N$), 2.04(s, 15H, C_5Me_5), 2.06(s, 3H), 1.77[s, 3H, $Me_2C_6H_3N{=}C(CH_2CMe_3)$], 0.98[s, 9H, $(Me_3CCH_2)C{=}NC_6H_3Me_2$]	b, 238.73[$C(CH_2CMe_3) = NC_6H_3Me_2$], 153.47–120.27[several phenyl, $C_6H_3Me_2N$, $C_6H_3Me_2N{=}C(CH_2CMe_3)$], 115.93($C_5Me_5$), 50.24[$(CH_2CMe_3)C{=}NC_6H_3Me_2$], 33.14[$(CH_2CMe_3)C{=}NC_6H_3Me_2$], 30.92[$(CH_2CMe_3)C{=}NC_6H_3Me_2$], 20(br,$Me_2C_6H_3N$), 18.78, 18.66[$Me_2C_6H_3N{=}C(CH_2CMe_3)$], 11.4($C_5Me_5$)
11	b, 7.15(m, 2H), 6.93[m, 3H, $(H_5C_6CH_2)C{=}NC_6H_3Me_2$], 7.10[m, 3H, $H_3C_6Me_2N{=}C(CH_2Ph)$], 6.87(d, 2H, $^3J_{\mathrm{H-H}} = 7.35$ Hz), 6.56(t, 1H, $^3J_{\mathrm{H-H}} = 7.35$ Hz, $H_3C_6Me_2N$), 4.41, 4.27[AB, 2H, $^2J_{\mathrm{H-H}} = 15.38$ Hz, $(PhCH_2)C{=}NC_6H_3Me_2$], 2.23(br, 6H,$Me_2C_6H_3N$), 2.02(s, 15H,C_5Me_5), 1.86(s, 3H), 1.76[s, 3H,$Me_2C_6H_3N{=}C(CH_2Ph)$]	b, 237.77[$C(CH_2Ph) = NC_6H_3Me_2$], 140.86–120.4[several phenyl, $C_6H_3Me_2N$, $C_6H_3Me_2N{=}C(CH_2C_6H_5)$], 115.86($C_5Me_5$), 43.00[$(CH_2Ph)C{=}NC_6H_3Me_2$], 19.3(br, $Me_2C_6H_3N$), 18.6, 18.34[$Me_2C_6H_3N{=}C(CH_2Ph)$], 11.31(C_5Me_5)
12	b, 8.05(m, 1H), 7.67(m, 1H), 7.43(m, 2H), 7.07(d, 1H), 6.98(t, 1H), 6.76[d, 1H, $\{H_4C_6(2\text{-}CH_2NMe_2)\}$ $C{=}NC_6H_3Me_2$], 6.88(d, 2H, $^3J_{\mathrm{H-H}} = 7.7$ Hz), 6.58(t, 1H, $^3J_{\mathrm{H-H}} = 7.7$ Hz, $H_3C_6Me_2N$), 2.75, 2.56 [AB, 2H, $^2J_{\mathrm{H-H}} = 13.50$ Hz, $\{H_4C_6(2\text{-}CH_2NMe_2)\}C{=}NC_6H_3Me_2$], 2.45(s, 6H, $Me_2C_6H_3N$), 2.05(s, 15H, C_5Me_5), 2.29(s, 3H), 1.38[s, 3H, $\{H_4C_6(2\text{-}CH_2NMe_2)\}C{=}NC_6H_3Me_2$], 1.94[s, 6H, $\{H_4C_6(2\text{-}CH_2NMe_2)\}C{=}NC_6H_3Me_2$]	b, 237.15[$\{H_4C_6(2\text{-}CH_2NMe_2)\}C = NC_6H_3Me_2$], 153.72–120.73[several phenyl, $C_6H_3Me_2N$, $\{H_4C_6(2\text{-}CH_2NMe_2)\}C{=}NC_6H_3Me_2$], 116.14($C_5$ Me_5), 60.17[$\{H_4C_6(2\text{-}CH_2NMe_2)\}C{=}NC_6H_3Me_2$], 45.07[$\{H_4C_6(2\text{-}CH_2NMe_2)\}C{=}NC_6H_3Me_2$], 20.27($Me_2C_6H_3N$), 20.06, 18.53[$\{H_4C_6(2\text{-}CH_2NMe_2)\}C{=}NC_6H_3Me_2$], 11.32($C_5Me_5$)
13	b, 6.92[m, 3H, $H_3C_6Me_2N{=}C(NMe_2)$], 6.86(d, 2H, $^3J_{\mathrm{H-H}} = 7.2$ Hz), 6.52(t, 1H, $^3J_{\mathrm{H-H}} = 7.2$ Hz, $H_3C_6Me_2N$), 3.46(s, 3H), 2.70[s, 3H, $H_3C_6Me_2N{=}C(NMe_2)$], 2.27(br, 6H,$Me_2C_6H_3N$), 2.09(s, 15H, C_5Me_5), 1.98(s, 3H), 1.88[s, 3H, $Me_2H_3C_6N{=}C(NMe_2)$]	b, 200.23[$C(NMe_2) = NC_6H_3Me_2$], 153.97–119.41[several phenyl, $C_6H_3Me_2N$, $C(NMe_2) = NC_6H_3Me_2$], 116(C_5Me_5), 45.37, 37.76[$H_3C_6Me_2N{=}C(NMe_2)$], 19.55(br,$Me_2C_6H_3N$), 19.27, 18.75[$Me_2C_6H_3N{=}C(NMe_2)$], 11.63(C_5Me_5)
14	b, 7.00(br, 3H, $H_3C_6Me_2N{=}C(CH_2SiMe_3)$], 6.87(d, 2H, $^3J_{\mathrm{H-H}} = 7.5$ Hz), 6.52(t, 1H, $^3J_{\mathrm{H-H}} = 7.5$ Hz, $H_3C_6Me_2N$), 3.45, 2.35[AB, 2H, $^2J_{\mathrm{H-H}} = 12.82$ Hz, $H_3C_6Me_2N{=}C(CH_2SiMe_3)$], 2.21(s, 6H, $Me_2H_3C_6N$), 1.94(s, 15H, C_5Me_5), 1.94[s, 6H, $H_3C_6Me_2N{=}C(CH_2SiMe_3)$], −0.12[s, 9H, $H_3C_6Me_2N{=}C(CH_2SiMe_3)$], −0.45(s, 9H, Ta–$CH_2SiMe_3$), −0.16, −0.67(AB, 2H, $^2J_{\mathrm{H-H}} = 12.45$ Hz, Ta–CH_2SiMe_3)	b, 244.78[$C(CH_2SiMe_3) = NC_6H_3Me_2$], 154.5–118.69[several phenyl, $C_6H_3Me_2N$, $C(CH_2SiMe_3) = NC_6H_3Me_2$], 112.7($C_5Me_5$), 28.38, 22.41[$C(CH_2SiMe_3) = NC_6H_3Me_2$, Ta–$CH_2SiMe_3$], 18.86(br, $Me_2H_3C_6N$), 19.30[$H_3C_6Me_2N{=}C(CH_2SiMe_3)$], 11.23($C_5Me_5$), 3.41, 0.77[$C(CH_2SiMe_3) = NC_6H_3Me_2$, Ta–$CH_2SiMe_3$]
15	b, 7.15(m, 4H), 7.05(m, 3H), 7.00(m, 1H), 6.83[m, 2H, $(H_5C_6Me_2CCH_2)C{=}NC_6H_3Me_2$, Ta–$CH_2CMe_2C_6H_5$], 7.06[m, 3H, $(H_5C_6Me_2CCH_2)C{=}NC_6H_3Me_2$], 6.90(d, 2H, $^3J_{\mathrm{H-H}} = 7.5$ Hz), 6.56(t, 1H, $^3J_{\mathrm{H-H}} = 7.5$ Hz, $H_3C_6Me_2N$), 4.16, 3.51 [AB, 2H, $^2J_{\mathrm{H-H}} = 16.85$ Hz, $(PhMe_2CCH_2)C{=}NC_6H_3Me_2$], 2.26(br, 6H, $Me_2C_6H_3N$), 1.85(s, 15H, C_5Me_5), 1.67(s, 3H), 1.53[s, 3H, $(PhMe_2CCH_2)C{=}NC_6H_3Me_2$], 1.50, 0.95(AB, 2H, $^2J_{\mathrm{H-H}} = 11.35$ Hz, Ta–CH_2CMe_2Ph), 1.22[br, 6H, Ta–CH_2CMe_2Ph], 1.21(s, 3H), 0.78[s, 3H, $(PhMe_2CCH_2)C{=}NC_6H_3Me_2$]	b, 244.68[[$C(CH_2CMe_2Ph) = NC_6H_3Me_2$], 159.15–119.26[several phenyl, $C_6H_3Me_2N$, $(H_5C_6Me_2CCH_2)C{=}NC_6H_3Me_2$, Ta–$CH_2CMe_2C_6H_5$], 113.24($C_5Me_5$), 58.42, 52.00(Ta–$CH_2CMe_2Ph$], 40.52, 38.81[$(PhMe_2CCH_2)C{=}NC_6H_3Me_2$], 33.75, 32.51, 31.30, 29.90[Ta–CH_2CMe_2Ph, $(PhMe_2CCH_2)C{=}NC_6H_3Me_2$], 20.71($Me_2H_3C_6N$), 18.97, 18.54[$(PhMe_2CCH_2)C{=}NC_6H_3Me_2$], 11.14($C_5Me_5$)
16	b, 7.00[m, 3H, $(Me_3CCH_2)C{=}NC_6H_3Me_2$], 6.88(d, 2H, $^3J_{\mathrm{H-H}} = 7.2$ Hz), 6.54(t, 1H, $^3J_{\mathrm{H-H}} = 7.2$ Hz, $H_3C_6Me_2N$), 3.76, 2.74[AB, 2H, $^2J_{\mathrm{H-H}} = 15.30$ Hz, $(Me_3CCH_2)C{=}NC_6H_3Me_2$], 2.29(s, 6H, $Me_2C_6H_3N$), 1.92(s, 15H, C_5Me_5), 1.95(s, 3H), 1.85[s, 3H, $(Me_3CCH_2)C{=}NC_6H_3Me_2$], 1.25, 0.50(AB, 2H, $^2J_{\mathrm{H-H}} = 14.10$ Hz, Ta–CH_2CMe_3), 0.86(s, 9H, Ta–CH_2CMe_3), 0.67[s, 9H, $(Me_3CCH_2)C{=}NC_6H_3Me_2$]	b, 246.47[$C(CH_2CMe_3) = NC_6H_3Me_2$], 154.55–119[several phenyl, $C_6H_3Me_2N$, $(Me_3CCH_2)C{=}NC_6H_3Me_2$], 113.06($C_5Me_5$), 57.75, 50.64[Ta–$CH_2CMe_3$, $(Me_3CCH_2)C{=}NC_6H_3Me_2$], 33.83, 33.11[Ta–$CH_2CMe_3$, $(Me_3CCH_2)C{=}NC_6H_3Me_2$], 35.79, 31.43 [Ta–$CH_2CMe_3$, $(Me_3CCH_2)C{=}NC_6H_3Me_2$], 20.55, 19.27[$(Me_3CCH_2)C{=}NC_6H_3Me_2$], 18.90(br, $Me_2C_6H_3N$), 11.18(C_5Me_5)
17	b, 7.10[m, 3H, $(PhCH_2)C{=}NC_6H_3Me_2$], 6.91(m, 2H), 6.74(m, 4H), 6.44(m, 3H), 6.33[m, 1H, $(H_5C_6CH_2)C{=}NC_6H_3Me_2$, Ta–$CH_2C_6H_5$], 6.96(d, 2H, $^3J_{\mathrm{H-H}} = 7.3$ Hz), 6.61(t, 1H, $^3J_{\mathrm{H-H}} = 7.3$ Hz, $H_3C_6Me_2N$), 4.32, 4.03[AB, 2H, $^2J_{\mathrm{H-H}} = 14.65$ Hz, $(PhCH_2)C{=}NC_6H_3Me_2$], 2.81, 1.81(AB, 2H, $^2J_{\mathrm{H-H}} = 11.35$ Hz, Ta–CH_2Ph), 2.34(br, 6H, $Me_2C_6H_3N$), 1.90(s, 15H, C_5Me_5), 1.72(s, 3H), 1.29[s, 3H, $(PhCH_2)C{=}NC_6H_3Me_2$]	b, 240.55[$C(CH_2Ph) = NC_6H_3Me_2$], 154.29–119.34[several phenyl, $C_6H_3Me_2N$, $(C_6H_5CH_2)C{=}NC_6H_3Me_2$, Ta–$CH_2C_6H_5$], 113.65($C_5Me_5$), 46.95, 42.17[$(C_6H_5CH_2)C{=}NC_6H_3Me_2$, Ta–$CH_2C_6H_5$], 19.94(br, $Me_2C_6H_3N$), 18.46, 18.30[$(C_6H_5CH_2)C{=}NC_6H_3Me_2$], 11.03($C_5Me_5$)
18	b, 7.66(m, 2H), 7.58(m, 2H), 7.44(m, 1H), 7.40(m, 2H), 6.92(m, 2H), 6.84(m, 3H), 6.73[m, 1H, $(H_5C_6)C{=}NC_6H_3Me_2$, Ta–C_6H_5], 6.85(d, 2H, $^3J_{\mathrm{H-H}} = 7.3$ Hz), 6.54(t, 1H, $^3J_{\mathrm{H-H}} = 7.3$ Hz, $H_3C_6Me_2N$), 2.25(s, 6H, $Me_2C_6H_3N$), 2.03(s, 15H, C_5Me_5), 1.86(s, 3H), 1.60[s, 3H, $(Ph)C{=}NC_6H_3Me_2$]	b, 232.57[$(Ph)C = NC_6H_3Me_2$], 181.52–119.30[several phenyl, $C_6H_3Me_2N$, $(C_6H_5)C{=}NC_6H_3Me_2$, Ta–C_6H_5], 114.91(C_5Me_5), 20.64($Me_2C_6H_3N$), 18.83, 18.45[$(Ph)C{=}NC_6H_3Me_2$], 12(C_5Me_5)

Table 2 (Continued)

	$^1\mathrm{H}$	$^{13}\mathrm{C}\{^1\mathrm{H}\}$
19	b^{b}, 1.98(s, 15H, $\mathrm{C_5}Me_5$), 0.16(s, 3H, Ta–Me), 0.05[s, 9H, $\mathrm{(CH_2Si}Me_3\mathrm{)C{=}NC_6H_3Me_2}$]	b^{b}, 241.67[$\mathrm{(CH_2SiMe_3)}C = \mathrm{NC_6H_3Me_2}$], 112.75($C_5\mathrm{Me_5}$), 20.35[$(C\mathrm{H_2SiMe_3)C{=}NC_6H_3Me_2}$], 19.07(Ta–Me), 10.96($\mathrm{C_5}Me_5$), 1.01[$\mathrm{(CH_2Si}Me_3\mathrm{)C{=}NC_6H_3Me_2}$]
20	b, 7.02[m, 3H, $\mathrm{(Me)C{=}NC_6}H_3\mathrm{Me_2}$], 6.87(d, 2H, $^3J_{\mathrm{H-H}} = 7.32$ Hz), 6.52(t, 1H, $^3J_{\mathrm{H-H}} = 7.32$ Hz, $H_3\mathrm{C_6Me_2N}$), 2.58[s, 3H, $(Me)\mathrm{C{=}NC_6H_3Me_2}$], 2.24(br, 3H), 2.18(br, 3H, $Me_2\mathrm{C_6H_3N}$), 1.93(s, 15H, $\mathrm{C_5}Me_5$), 1.88(s, 3H), 1.85[s, 3H, $\mathrm{(Me)C{=}NC_6H_3}Me_2$], -0.43(s, 9H, Ta–$\mathrm{CH_2Si}Me_3$), -0.08, -0.64(AB, 2H, $^2J_{\mathrm{H-H}} = 12.45$ Hz, Ta–$\mathrm{C}H_2\mathrm{SiMe_3}$)	b, 243[$\mathrm{(Me)}C = \mathrm{NC_6H_3Me_2}$], 154.24–118.97[several phenyl, $C_6\mathrm{H_3Me_2N}$, $\mathrm{(Me)C{=}N}C_6\mathrm{H_3Me_2}$], 112.87($C_5\mathrm{Me_5}$), 23.51(Ta–$C\mathrm{H_2SiMe_3}$), 20.45[$(Me)\mathrm{C{=}NC_6H_3Me_2}$], 19.62, 18.92(br, $Me_2\mathrm{C_6H_3N}$), 18.63, 18.36[$\mathrm{(Me)C{=}NC_6H_3}Me_2$], 11($\mathrm{C_5}Me_5$), 3.28(Ta–$\mathrm{CH_2Si}Me_3$)
21	b^{b}, 4.10[AB, 2H, $^2J_{\mathrm{H-H}} = 14.4$ Hz, $\mathrm{(C_6H_5C}H_2\mathrm{)C{=}NC_6H_3Me_2}$], 1.90(s, 15H, $\mathrm{C_5}Me_5$), 0.11(s, 3H, Ta–Me)	
22	b, 6.94(m, 2H), 6.83(d, 2H), 6.59(t, 1H), 6.52(m, 1H), 6.45[t, 2H, $\mathrm{(Me)C{=}NC_6}H_3\mathrm{Me_2}$, Ta–$\mathrm{CH_2C_6}H_5$], 6.75(d, 2H, $^3J_{\mathrm{H-H}} = 7.2$ Hz), 6.27(t, 1H, $^3J_{\mathrm{H-H}} = 7.2$ Hz, $H_3\mathrm{C_6Me_2N}$), 2.51(br, 3H), 2.13(br, 3H, $Me_2\mathrm{C_6H_3N}$), 2.48, 1.82 (AB, 2H, $^2J_{\mathrm{H-H}} = 11.72$ Hz, Ta–$\mathrm{C}H_2\mathrm{Ph}$), 2.44[s, 3H, $(Me)\mathrm{C{=}NC_6H_3Me_2}$], 2(s, 15H, $\mathrm{C_5}Me_5$), 1.80(s, 3H), 1.25[s, 3H, $\mathrm{(Me)C{=}NC_6H_3}Me_2$]	b, 242.32[$\mathrm{(Me)}C = \mathrm{NC_6H_3Me_2}$], 151.70–119.28 [several phenyl, $C_6\mathrm{H_3Me_2N}$, $\mathrm{(Me)C{=}N}C_6\mathrm{H_3Me_2}$, Ta–$\mathrm{CH_2}C_6\mathrm{H_5}$], 113.16($C_5\mathrm{Me_5}$), 46.54(Ta–$C\mathrm{H_2Ph}$), 19.88[$(Me)\mathrm{C{=}NC_6H_3Me_2}$], 18.41, 17.97 [$\mathrm{(Me)C{=}NC_6H_3}Me_2$], 17.60(br, $Me_2\mathrm{C_6H_3N}$), 10.91($\mathrm{C_5}Me_5$)
23	b, 7.12[m, 3H, $\mathrm{(PhMe_2CCH_2)C{=}NC_6}H_3\mathrm{Me_2}$], 7.13(m, 1H), 7.03 (m, 2H), 6.90(m, 1H), 6.74[m, 1H, $(H_5\mathrm{C_6Me_2CCH_2)C{=}NC_6H_3Me_2}$], 6.87(d, 2H, $^3J_{\mathrm{H-H}} = 7.5$ Hz), 6.40(t, 1H, $^3J_{\mathrm{H-H}} = 7.5$ Hz, $H_3\mathrm{C_6Me_2N}$), 3.08, 3.04[AB, 2H, $^2J_{\mathrm{H-H}} = 13.5$ Hz, $(\mathrm{C}H_2\mathrm{CMe_2Ph)C{=}NC_6H_3Me_2}$], 2.10(br, 6H, $Me_2\mathrm{C_6H_3N}$), 1.80(s, 15H, $\mathrm{C_5}Me_5$), 1.79(s, 3H), 1.50 [s, 3H,$\mathrm{(CH_2CMe_2Ph)C{=}NC_6H_3}Me_2$], 1.63(s, 3H), 1.10[s, 3H, $\mathrm{(CH_2C}Me_2\mathrm{Ph)C{=}NC_6H_3Me_2}$], 0.00(s, Ta–$Me$)	b, 239.71[$\mathrm{(CH_2CMe_2Ph)}C = \mathrm{NC_6H_3Me_2}$], 154.95–118.69[several phenyl, $C_6\mathrm{H_3Me_2N}$, $\mathrm{(CH_2CMe_2}C_6\mathrm{H_5)C{=}N}C_6\mathrm{H_3Me_2}$], 113.80($C_5\mathrm{Me_5}$), 49.70[$(C\mathrm{H_2CMe_2Ph)C{=}NC_6H_3Me_2}$], 38.87[$\mathrm{(CH_2}C\mathrm{Me_2Ph)C{=}NC_6H_3Me_2}$], 30.07, 29.42[$\mathrm{(CH_2C}Me_2\mathrm{Ph)C{=}NC_6H_3Me_2}$], 21.82(Ta–$Me$), 20.02($Me_2\mathrm{C_6H_3N}$), 18.44, 18.19[$\mathrm{(CH_2CMe_2Ph)C{=}NC_6H_3}Me_2$], 11.13($\mathrm{C_5}Me_5$)
24	b^{b}, 2.80[s, 3H, $(Me)\mathrm{C{=}NC_6H_3Me_2}$], 2.14(s, 15H, $\mathrm{C_5}Me_5$), 1.86, 1.44(AB, 2H, $^2J_{\mathrm{H-H}} = 13.5$ Hz, Ta–$\mathrm{C}H_2\mathrm{CMe_2Ph}$)	b^{b}, 244.08[$\mathrm{(Me)}C = \mathrm{NC_6H_3Me_2}$], 113.44($C_5\mathrm{Me_5}$), 60.94(Ta–$C\mathrm{H_2CMe_2Ph}$), 20.62[$(Me)\mathrm{C{=}NC_6H_3Me_2}$], 11.18($\mathrm{C_5}Me_5$)
25	b, 7.03[m, 3H, $\mathrm{(Me_3CCH_2)C{=}NC_6}H_3\mathrm{Me_2}$], 6.85(d, 2H, $^3J_{\mathrm{H-H}} = 7.32$ Hz), 6.50(t, 1H, $^3J_{\mathrm{H-H}} = 7.32$ Hz, $H_3\mathrm{C_6Me_2N}$), 2.77, 2.66[AB, 2H, $^2J_{\mathrm{H-H}} = 12.68$ Hz, $\mathrm{(Me_3CC}H_2\mathrm{)C{=}NC_6H_3Me_2}$], 2.44(br, 6H,$Me_2\mathrm{C_6H_3N}$), 1.95(s, 15H, $\mathrm{C_5}Me_5$), 2.01(s, 3H), 1.65 [s, 3H, $\mathrm{(Me_3CCH_2)C{=}NC_6H_3}Me_2$], 1.05[s, 9H, $(Me_3\mathrm{CCH_2)C{=}NC_6H_3Me_2}$], 0.13(s, 3H, Ta–$Me$)	b, 239.95[$\mathrm{(Me_3CCH_2)}C = \mathrm{NC_6H_3Me_2}$], 155.05–118.60[several phenyl, $C_6\mathrm{H_3Me_2N}$, $\mathrm{(Me_3CCH_2)C{=}N}C_6\mathrm{H_3Me_2}$], 112.95($C_5\mathrm{Me_5}$), 49.44[$\mathrm{(Me_3C}C\mathrm{H_2)C{=}NC_6H_3Me_2}$], 32.74[$\mathrm{(Me_3}C\mathrm{CH_2)C{=}NC_6H_3Me_2}$], 30.83[$(Me_3\mathrm{CCH_2)C{=}NC_6H_3Me_2}$], 21.84(Ta–$Me$), 19.97(br, $Me_2\mathrm{C_6H_3N}$), 18.50, 18.23[$\mathrm{(Me_3CCH_2)C{=}NC_6H_3}Me_2$], 11.19($\mathrm{C_5}Me_5$)
26	b^{b}, 2.61[s, 3H, $(Me)\mathrm{C{=}NC_6H_3Me_2}$], 1.94(s, 15H, $\mathrm{C_5}Me_5$)	b^{b}, 240.45[$\mathrm{(Me)}C = \mathrm{NC_6H_3Me_2}$], 115.54($C_5\mathrm{Me_5}$), 35.58[$(Me)\mathrm{C{=}NC_6H_3Me_2}$], 11.16($\mathrm{C_5}Me_5$)
27	b, 7.62(m, 3H), 7.41(m, 2H), 7.07(m, 1H), 7.02(t, 1H), 6.90[m, 2H, $(\mathrm{C_6}H_5\mathrm{)C{=}NC_6}H_3\mathrm{Me_2}$], 6.85(d, 2H, $^3J_{\mathrm{H-H}} = 7.70$ Hz), 6.50(t, 1H, $^3J_{\mathrm{H-H}} = 7.70$ Hz, $H_3\mathrm{C_6Me_2N}$), 2.26(br, 6H, $Me_2\mathrm{C_6H_3N}$), 1.98(s, 15H, $\mathrm{C_5}Me_5$), 1.96(s, 3H), 1.57 [s, 3H, $\mathrm{(C_6H_5)C{=}NC_6H_3}Me_2$], 0.23(s, 3H, Ta–$Me$)	b, 232.34[$\mathrm{(C_6H_5)}C = \mathrm{NC_6H_3Me_2}$], 154.96–118.74[several phenyl, $C_6\mathrm{H_3Me_2N}$, $(C_6\mathrm{H_5)C{=}N}C_6\mathrm{H_3Me_2}$], 113.08($C_5\mathrm{Me_5}$), 19.87(Ta–$Me$), 18.68($Me_2\mathrm{C_6H_3N}$), 18.22, 18.07[$\mathrm{(C_6H_5)C{=}NC_6H_3}Me_2$], 11.20($\mathrm{C_5}Me_5$)
28	b^{b}, 2.64[s, 3H, $(Me)\mathrm{C{=}NC_6H_3Me_2}$], 1.90(s, 15H, $\mathrm{C_5}Me_5$)	b^{b}, 240.48[$\mathrm{(Me)}C = \mathrm{NC_6H_3Me_2}$], 114.11($C_5\mathrm{Me_5}$), 20.65[$(Me)\mathrm{C{=}NC_6H_3Me_2}$], 11.30($\mathrm{C_5}Me_5$)
29	b, 7.92(m, 1H), 7.64(m, 1H), 7.37[m, 2H, $\{H_4\mathrm{C_6(2\text{-}CH_2NMe_2)\}C{=}NC_6H_3Me_2}$], 7.04(d, 1H), 6.96(t, 1H), 6.77[d, 1H, $^3J_{\mathrm{H-H}} = 7.59$ Hz, $\mathrm{\{H_4C_6(2\text{-}CH_2NMe_2)\}C{=}NC_6}H_3\mathrm{Me_2}$], 6.86(d, 2H, $^3J_{\mathrm{H-H}} = 7.40$ Hz), 6.52(t, 1H, $^3J_{\mathrm{H-H}} = 7.40$ Hz, $H_3\mathrm{C_6Me_2N}$), 2.80, 2.74[AB, 2H, $^2J_{\mathrm{H-H}} = 14.85$ Hz, $\mathrm{\{H_4C_6(2\text{-}C}H_2\mathrm{NMe_2)\}C{=}NC_6H_3Me_2}$], 2.34(s, 6H, $Me_2\mathrm{C_6H_3N}$), 2.15(s, 3H), 1.35[s, 3H, $\mathrm{\{H_4C_6(2\text{-}CH_2NMe_2)\}C{=}NC_6H_3}Me_2$], 1.97[s, 6H, $\mathrm{\{H_4C_6(2\text{-}CH_2N}Me_2\mathrm{)\}\text{-}C{=}NC_6H_3Me_2}$], 1.96(s, 15H, $\mathrm{C_5}Me_5$), 0.35(s, 3H, Ta–Me)	b, 239.86[$\mathrm{\{H_4C_6(2\text{-}CH_2NMe_2)\}}C = \mathrm{NC_6H_3Me_2}$], 155.19–119.06[several phenyl, $C_6\mathrm{H_3Me_2N}$, $\mathrm{\{H_4}C_6\mathrm{(2\text{-}CH_2NMe_2)\}C{=}N}C_6\mathrm{H_3Me_2}$], 113.10 ($C_5\mathrm{Me_5}$), 60.24[$\mathrm{\{H_4C_6(2\text{-}}C\mathrm{H_2NMe_2)\}C{=}NC_6H_3Me_2}$], 45.14[$\mathrm{\{H_4C_6(2\text{-}CH_2N}Me_2\mathrm{)\}C{=}NC_6H_3Me_2}$], 20.13(Ta–$Me$), 20.58($Me_2\mathrm{C_6H_3N}$), 19.39, 18.62[$\mathrm{\{H_4C_6(2\text{-}CH_2NMe_2)\}C{=}NC_6H_3}Me_2$], 11.10($\mathrm{C_5}Me_5$)
30	b, 6.90[m, 3H, $\mathrm{(Me_2N)C{=}NC_6}H_3\mathrm{Me_2}$], 6.84(d, 2H, $^3J_{\mathrm{H-H}} = 7.20$ Hz), 6.47(t, 1H, $^3J_{\mathrm{H-H}} = 7.20$ Hz, $H_3\mathrm{C_6Me_2N}$), 3.47(s, 3H), 2.67[s, 3H, $(Me_2\mathrm{N)C{=}NC_6H_3Me_2}$], 2.17(br, 6H, $Me_2\mathrm{C_6H_3N}$), 2.00(s, 15H, $\mathrm{C_5}Me_5$), 1.92(s, 3H), 1.79[s, 3H, $\mathrm{(Me_2N)C{=}NC_6H_3}Me_2$], -0.028(s, 3H, Ta–Me).	b, 199.69[$\mathrm{(Me_2N)}C = \mathrm{NC_6H_3Me_2}$], 155.45–117.73[several phenyl, $C_6\mathrm{H_3Me_2N}$, $\mathrm{(Me_2N)C{=}N}C_6\mathrm{H_3Me_2}$], 112.87($\mathrm{C_5}Me_5$), 45.54, 37.32[$(Me_2\mathrm{N)C{=}NC_6H_3Me_2}$], 20.09(Ta–$Me$), 19.55(br, $Me_2\mathrm{C_6H_3N}$), 19.07, 18.60[$\mathrm{(Me_2N)C{=}NC_6H_3}Me_2$], 11.34($\mathrm{C_5}Me_5$)

Table 2 (Continued)

	^{1}H	$^{13}C\{^{1}H\}$
31	a, 7.08(d, 2H, $^{3}J_{H-H} = 7.8$ Hz), 6.74(t, 1H, $^{3}J_{H-H} = 7.8$ Hz, $\mathit{H}_3C_6Me_2N$), 3.68, 2.43 [AB, 2H, $^{2}J_{H-H} = 11.1$ Hz, $(Me_3SiC\mathit{H}_2)C{=}O$], 2.48(s, 6H, $\mathit{Me}_2C_6H_3N$), 1.69(s, 15H, $C_5\mathit{Me}_5$), 0.47, 0.19(AB, 2H, $^{2}J_{H-H} = 11$ Hz, Ta–$C\mathit{H}_2SiMe_3$), 0.41[s, 9H, $(\mathit{Me}_3SiCH_2)C{=}O$], 0.05(s, 9H, Ta–$CH_2Si\mathit{Me}_3$)	a, 317.78[$(Me_3SiCH_2)\mathit{C} = O$], 154.7, 131.17, 127.44, 120.53(C_i, C_o, C_m, C_p, $\mathit{C}_6H_3Me_2N$), 113.5($C_5\mathit{Me}_5$), 37.92[$(Me_3Si\mathit{C}H_2)C{=}O$], 29.11(Ta–$\mathit{C}H_2SiMe_3$), 19.82($\mathit{Me}_2C_6H_3N$), 10.9($C_5\mathit{Me}_5$), 4.37[$(\mathit{Me}_3SiCH_2)C{=}O$], 0.096(Ta–$CH_2Si\mathit{Me}_3$)
32	a, 7.68(d, 2H), 7.26(m, 4H), 7.11(m, 2H), 7.03[m, 2H, $(\mathit{H}_5C_6Me_2CCH_2)C{=}O$, Ta–$CH_2CMe_2C_6\mathit{H}_5$], 7.08(d, 2H, $^{3}J_{H-H} = 7.5$ Hz), 6.78(t, 1H, $^{3}J_{H-H} = 7.5$ Hz, $\mathit{H}_3C_6Me_2N$), 3.98, 3.4[AB, 2H, $^{2}J_{H-H} = 20.5$ Hz, $(PhMe_2CC\mathit{H}_2)C{=}O$], 2.34(s, 6H, $\mathit{Me}_2C_6H_3N$), 1.60(s, 3H), 1.56[s, 3H, $(Ph\mathit{Me}_2CCH_2)C{=}O$], 1.78, 1.6(AB, 2H, $^{2}J_{H-H} = 13.5$ Hz, Ta–$C\mathit{H}_2CMe_2Ph$), 1.57(s, 15H, $C_5\mathit{Me}_5$), 1.37(s, 3H), 1.32(s, 3H, Ta–$CH_2C\mathit{Me}_2Ph$)	a, 315.4[$(PhMe_2CCH_2)\mathit{C} = O$], 157.87–120.79[several phenyl, $\mathit{C}_6H_3Me_2N$, $(\mathit{C}_6H_5Me_2CCH_2)C{=}O$, Ta–$CH_2CMe_2\mathit{C}_6H_5$], 113.62($C_5\mathit{Me}_5$), 61.7, 58.32[$(PhMe_2C\mathit{C}H_2)C{=}O$, Ta–$\mathit{C}H_2CMe_2Ph$], 42.73, 37.83[$(PhMe_2\mathit{C}CH_2)C{=}O$, Ta–$CH_2\mathit{C}Me_2Ph$], 34.9, 33.05, 28.93, 28.3[$(Ph\mathit{Me}_2CCH_2)C{=}O$, Ta–$CH_2C\mathit{Me}_2Ph$], 20.48($\mathit{Me}_2C_6H_3N$), 10.73($C_5\mathit{Me}_5$)
33	b, 6.88(d, 2H, $^{3}J_{H-H} = 7.5$ Hz), 6.56 (t, 1H, $^{3}J_{H-H} = 7.5$ Hz, $\mathit{H}_3C_6Me_2N$), 3.8, 3.07[AB, 2H, $^{2}J_{H-H} = 20$ Hz, $(Me_3CC\mathit{H}_2)C{=}O$], 2.22(s, 6H, $\mathit{Me}_2C_6H_3N$), 1.87(s, 15H, $C_5\mathit{Me}_5$), 1.24, 1.01(AB, 2H, $^{2}J_{H-H} = 13.04$ Hz, Ta–$C\mathit{H}_2CMe_3$), 1.10(s, 9H, Ta–$CH_2C\mathit{Me}_3$), 0.98[s, 9H, $(\mathit{Me}_3CCH_2)C{=}O$]	b, 317.47[$(Me_3CCH_2)\mathit{C} = O$], 154.18, 131.54, 126.75, 119.58(C_i, C_o, C_m, C_p, $\mathit{C}_6H_3Me_2N$), 113.5($C_5\mathit{Me}_5$), 62.11, 57.28[$(Me_3C\mathit{C}H_2)C{=}O$, Ta–$\mathit{C}H_2CMe_3$], 36.02, 31.66[$(Me_3\mathit{C}CH_2)C{=}O$, Ta–$CH_2\mathit{C}Me_3$], 35.28, 29.65[$(\mathit{Me}_3CCH_2)C{=}O$, Ta–$CH_2C\mathit{Me}_3$], 20.05($\mathit{Me}_2C_6H_3N$), 10.91 ($C_5\mathit{Me}_5$)
34	a, 7.53(d, 2H), 7.12(m, 5H), 7.00 (m, 2H), 6.80[m, 1H, $(\mathit{H}_5C_6CH_2)C{=}O$, Ta–$CH_2C_6\mathit{H}_5$], 7.06(d, 2H, $^{3}J_{H-H} = 7.2$ Hz), 6.77(t, 1H, $^{3}J_{H-H} = 7.2$ Hz, $\mathit{H}_3C_6Me_2N$), 4.30, 4.02[AB, 2H, $^{2}J_{H-H} = 17.58$ Hz, $(PhC\mathit{H}_2)C{=}O$], 3.05, 2.37(AB, 2H, $^{2}J_{H-H} = 11.35$ Hz, Ta–$C\mathit{H}_2Ph$), 2.33(s, 6H,$\mathit{Me}_2C_6H_3N$), 1.64(s, 15H, $C_5\mathit{Me}_5$)	a, 313.26[$(PhCH_2)\mathit{C} = O$], 153.58–122.03[several phenyl, $\mathit{C}_6H_3Me_2N$, $(H_5\mathit{C}_6CH_2)C{=}O$, Ta–$CH_2\mathit{C}_6H_5$], 117.31($C_5\mathit{Me}_5$), 58.57[$(Ph\mathit{C}H_2)C{=}O$], 49.97(Ta–$\mathit{C}H_2Ph$), 19.4 ($\mathit{Me}_2C_6H_3N$), 10.57($C_5\mathit{Me}_5$)
35	a, 7.2(m, 2H), 7.09(t, 2H), 7.01[m, 1H, $(\mathit{H}_5C_6Me_2CCH_2)C{=}O$], 7.00(d, 2H, $^{3}J_{H-H} = 7.2$ Hz), 6.71(t, 1H, $^{3}J_{H-H} = 7.2$ Hz, $\mathit{H}_3C_6Me_2N$), 3.62[q, 2H, $^{2}J_{H-H} = 19.5$ Hz, $(PhMe_2CC\mathit{H}_2)C{=}O$], 2.46(s, 6H, $\mathit{Me}_2C_6H_3N$), 1.72(s, 15H, $C_5\mathit{Me}_5$), 1.37(s, 3H), 1.23[s, 3H, $(Ph\mathit{Me}_2CCH_2)C{=}O$]	a, 315.17[$(PhMe_2CCH_2)\mathit{C} = O$], 153.25–122.2[several phenyl, $\mathit{C}_6H_3Me_2N$, $(H_5\mathit{C}_6Me_2CCH_2)C{=}O$], 116.16($C_5\mathit{Me}_5$), 58.48[$(PhMe_2C\mathit{C}H_2)C{=}O$], 38.31[$(PhMe_2\mathit{C}CH_2)C{=}O$], 29.37, 27.53[$(Ph\mathit{Me}_2CCH_2)C{=}O$], 19.54($\mathit{Me}_2C_6H_3N$),10.91 ($C_5\mathit{Me}_5$)
36	b, 6.86(d, 2H, $^{3}J_{H-H} = 7.4$ Hz), 6.55 (t, 1H, $^{3}J_{H-H} = 7.2$ Hz, $\mathit{H}_3C_6Me_2N$), 3.46(s, 3H), 3.26[s, 3H, $(\mathit{Me}_2N)C{=}O$], 2.31(s, 6H, $\mathit{Me}_2C_6H_3N$), 2.06(s, 15H,$C_5\mathit{Me}_5$)	b, 227.97[$(Me_2N)\mathit{C} = O$], 153.14, 131.92, 126.6, 120.93(C_i, C_o, C_m, C_p, $\mathit{C}_6H_3Me_2N$), 116.76 ($C_5\mathit{Me}_5$), 41.22, 37.61[$(\mathit{Me}_2N)C{=}O$], 19.33($\mathit{Me}_2C_6H_3N$), 11.4($C_5\mathit{Me}_5$)
37	a, 7.22(m, 2H), 7.11(m, 2H), 6.98[m, 1H, $(\mathit{H}_5C_6Me_2CCH_2)C{=}O$], 7.06(d, 2H, $^{3}J_{H-H} = 7.5$ Hz), 6.75(t, 1H, $^{3}J_{H-H} = 7.5$ Hz, $\mathit{H}_3C_6Me_2N$), 3.7 [q, 2H, $^{2}J_{H-H} = 19.5$ Hz, $(PhMe_2CC\mathit{H}_2)C{=}O$], 2.43(s, 6H, $\mathit{Me}_2C_6H_3N$), 1.65(s, 15H, $C_5\mathit{Me}_5$), 1.40(s, 3H), 1.28[s, 3H, $(Ph\mathit{Me}_2CCH_2)C{=}O$], 0.98(s, 3H, Ta–$\mathit{Me}$)	a, 319.38[$(PhMe_2CCH_2)\mathit{C} = O$], 154.93–120.72[several phenyl, $\mathit{C}_6H_3Me_2N$, $(H_5\mathit{C}_6Me_2CCH_2)C{=}O$], 113.33($C_5\mathit{Me}_5$), 58.28 [$(PhMe_2C\mathit{C}H_2)C{=}O$], 38.28[$(PhMe_2\mathit{C}CH_2)C{=}O$], 29.71, 27.76[$(Ph\mathit{Me}_2CCH_2)C{=}O$], 24.93(Ta–$\mathit{Me}$), 19.63($\mathit{Me}_2C_6H_3N$), 10.68($C_5\mathit{Me}_5$)
38	a, 7.06(d, 2H, $^{3}J_{H-H} = 7.5$ Hz), 6.75 (t, 1H, $^{3}J_{H-H} = 7.5$ Hz, $\mathit{H}_3C_6Me_2N$), 3.43, 3.06[AB, 2H, $^{2}J_{H-H} = 19$ Hz, $(Me_3CC\mathit{H}_2)C{=}O$], 2.44(s, 6H, $\mathit{Me}_2C_6H_3N$), 1.72(s, 15H,$C_5\mathit{Me}_5$), 1.06(s, 3H, Ta–Me), 0.94[s, 9H, $(\mathit{Me}_3CCH_2)C{=}O$]	a, 320.66[$(Me_3CCH_2)\mathit{C} = O$], 131.72, 128.29, 127.32, 120.73(C_i, C_o, C_m, C_p, $\mathit{C}_6H_3Me_2N$), 113.31($C_5\mathit{Me}_5$), 57.48[$(Me_3C\mathit{C}H_2)C{=}O$], 31.86[$(Me_3\mathit{C}CH_2)C{=}O$], 29.75[$(\mathit{Me}_3CCH_2)C{=}O$], 24.76(Ta–$\mathit{Me}$), 19.66($\mathit{Me}_2C_6H_3N$), 10.78($C_5\mathit{Me}_5$)
39	a, 6.98(d, 2H, $^{3}J_{H-H} = 7.2$ Hz), 6.71 (t, 1H, $^{3}J_{H-H} = 7.2$ Hz, $\mathit{H}_3C_6Me_2N$), 3.4, 2.87[AB, 2H, $^{2}J_{H-H} = 20$ Hz, $(Me_3CC\mathit{H}_2)CO$], 2.47(s, 6H, $\mathit{Me}_2C_6H_3N$), 1.78(s, 15H, $C_5\mathit{Me}_5$), 0.89[s, 9H, $(\mathit{Me}_3CCH_2)CO$]	a, 153.23[$(Me_3CCH_2)\mathit{C}O$], 132.43, 128.29, 127.3, 122.22(C_i, C_o, C_m, C_p, $\mathit{C}_6H_3Me_2N$), 116.05 ($C_5\mathit{Me}_5$), 57.53[$(Me_3C\mathit{C}H_2)CO$], 31.87[$(Me_3\mathit{C}CH_2)CO$], 29.56[$(\mathit{Me}_3CCH_2)CO$], 19.62($\mathit{Me}_2C_6H_3N$), 11.02($C_5\mathit{Me}_5$)
40	a, 7.12(d, 1H), 6.92(t, 1H), 6.70(d, 1H), 6.63[d, 1H, $\{\mathit{H}_4C_6(2\text{-}CH_2NMe_2)\}CO$], 7.12(d, 2H, $^{3}J_{H-H} = 7.5$ Hz), 6.77(t, 1H, $^{3}J_{H-H} = 7.5$ Hz, $\mathit{H}_3C_6Me_2N$), 3.22, 3.00[AB, 2H, $^{2}J_{H-H} = 13.5$ Hz, $\{H_4C_6(2\text{-}C\mathit{H}_2NMe_2)\}CO$], 2.53[s, br, 6H, $\{H_4C_6(2\text{-}CH_2N\mathit{Me}_2)\}CO$], 2.17 (s, br, 6H, $\mathit{Me}_2C_6H_3N$), 2.03(s, 15H, $C_5\mathit{Me}_5$), 0.53(s, 3H, Ta–Me)	a, 155.38[$\{H_4C_6(2\text{-}CH_2NMe_2)\}\mathit{C}O$], 147.4–119.53[several phenyl, $\mathit{C}_6H_3Me_2N$, $\{H_4\mathit{C}_6(2\text{-}CH_2NMe_2)\}CO$], 113.19($C_5\mathit{Me}_5$), 66.49[$\{H_4C_6(2\text{-}\mathit{C}H_2NMe_2)\}CO$], 45.59[br, $\{H_4C_6(2\text{-}CH_2N\mathit{Me}_2)\}CO$], 19.8(br,$\mathit{Me}_2C_6H_3N$), 18.83(Ta–$\mathit{Me}$), 11.18($C_5\mathit{Me}_5$)
41	a, 6.87(m, 2H), 6.81[m, 1H, $(Me_3CCH_2)C{=}NC_6\mathit{H}_3Me_2$], 2.74[q, 2H, $^{2}J_{H-H} = 12.82$ Hz, $(Me_3CC\mathit{H}_2)C{=}NC_6H_3Me_2$], 2.58(s, 3H), 1.54[s, 3H, $(Me_3CCH_2)C{=}NC_6H_3\mathit{Me}_2$], 2.01(s, 15H, $C_5\mathit{Me}_5$), 0.95[$(\mathit{Me}_3CCH_2)C{=}NC_6H_3Me_2$]	a, 240.49[$(Me_3CCH_2)\mathit{C} = NC_6H_3Me_2$], 140[$C_i$, $(Me_3CCH_2)C{=}N\mathit{C}_6H_3Me_2$], 133.85, 129.72, 128.58, 127.46, 127.12[$(Me_3CCH_2)C{=}N\mathit{C}_6H_3Me_2$], 117.44($C_5\mathit{Me}_5$), 47.68[$(Me_3C\mathit{C}H_2)C{=}NC_6H_3Me_2$], 34.06[$(Me_3\mathit{C}CH_2)C{=}NC_6H_3Me_2$], 30.54 [$(\mathit{Me}_3CCH_2)C{=}NC_6H_3Me_2$], 19.22, 18.83[$(Me_3CCH_2)C{=}NC_6H_3\mathit{Me}_2$], 11.53($C_5\mathit{Me}_5$)
42	a, 7.94(d, 2H), 7.78(br, 2H), 7.21(t, 2H), 7.05(m, 2H), 6.97[m, 2H, $(\mathit{H}_5C_6)C{=}NC_6H_3Me_2$, Ta–$C_6\mathit{H}_5$], 6.94(d, 1H, $^{3}J_{H-H} = 7.5$ Hz), 6.81(t, 1H, $^{3}J_{H-H} = 7.5$ Hz), 6.52[d, 1H, $^{3}J_{H-H} = 7.5$ Hz, $(Ph)C{=}NC_6\mathit{H}_3Me_2$], 2.00(s, 15H, $C_5\mathit{Me}_5$), 2.04(s, 3H), 1.74[s, 3H, $(Ph)C{=}NC_6H_3\mathit{Me}_2$]	a, 235.9[$(Ph)\mathit{C} = NC_6H_3Me_2$], 182.36–125.49[several phenyl, $(H_5\mathit{C}_6)C{=}N\mathit{C}_6H_3Me_2$, Ta–$C_6\mathit{H}_5$], 116($C_5\mathit{Me}_5$), 18.64, 18.31[$(Ph)C{=}NC_6H_3\mathit{Me}_2$], 11.65($C_5\mathit{Me}_5$)

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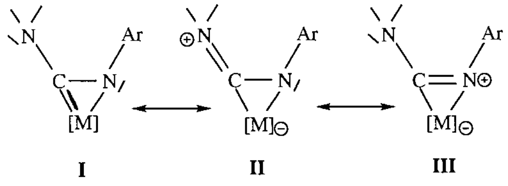
[a] Chemical shifts in δ: a, benzene-d_6; b, chloroform-d.

[b] The most relevant shifts.



Scheme 3.

tively, however in the η^2-iminocarbamoyl complexes are observed at δ 200.23 (**13**) and 199.69 (**30**). The shielding of these resonances is due to the positive charge deslocalisation between two nitrogen atoms in η^2-iminocarbamoyl complexes in agreement with the major participation of the resonance forms II and III (Scheme 3), proposed by Chisholm et al. [18] in order to explain the result obtained in the insertion process of 2,6-$Me_2C_6H_3NC$ into Mo–NMe_2 bonds of $Mo(NMe_2)_4$. Finally, the ^1H- and $^{13}C\{^1H\}$-NMR spectra of the complexes **12** and **29**, which contain the 2-[(dimethylamino)methyl)]phenyl ligand, able to form cyclometalated species via coordination of the nitrogen atom to the metal centre [19], show the equivalence of methyl groups in the NMe_2 moiety, consistent with an aryl ligand σ-bonded to metal centre with non-coordinated amine functionality.

*2.1.1. X-ray structures of [MCpCl(NAr){η^2-C(Me)=NAr)}] (Ar = 2,6-$Me_2C_6H_3$; M = Nb, Cp = η^5-$C_5H_4SiMe_3$, **1**; M = Ta, Cp = η^5-C_5Me_5, **7**)*

The molecular structure of compound **1** is shown in Fig. 1 while **7** is in Fig. 2. Selected bond distances and angles are presented in Tables 3 and 4, respectively. Both compounds are monomers, and show the metal centres within a classical four-legged stool environment, or three-legged if we take into consideration the centroid of the N(1)–C(21) and N(1)–C(2) bonds. The distances for both metal centres, niobium [20] and tantalum [5,13c,21] to the cyclopentadienyl ring carbons and the internal cyclopentadienyl parameters are in the normal range. Distances from the metal centres to the imido nitrogen atom, Nb(1)–N(2) 1.781(2) and Ta(1)–N(2) 1.795(6) Å are similar to other imido derivatives found in the literature [4a,5,20b]. Distances and angles around the carbon and nitrogen atoms of the iminoacyl groups are typical of carbon–nitrogen double bond [N(1)–C(21) 1.265(3) for **1**, N(1)–C(2)

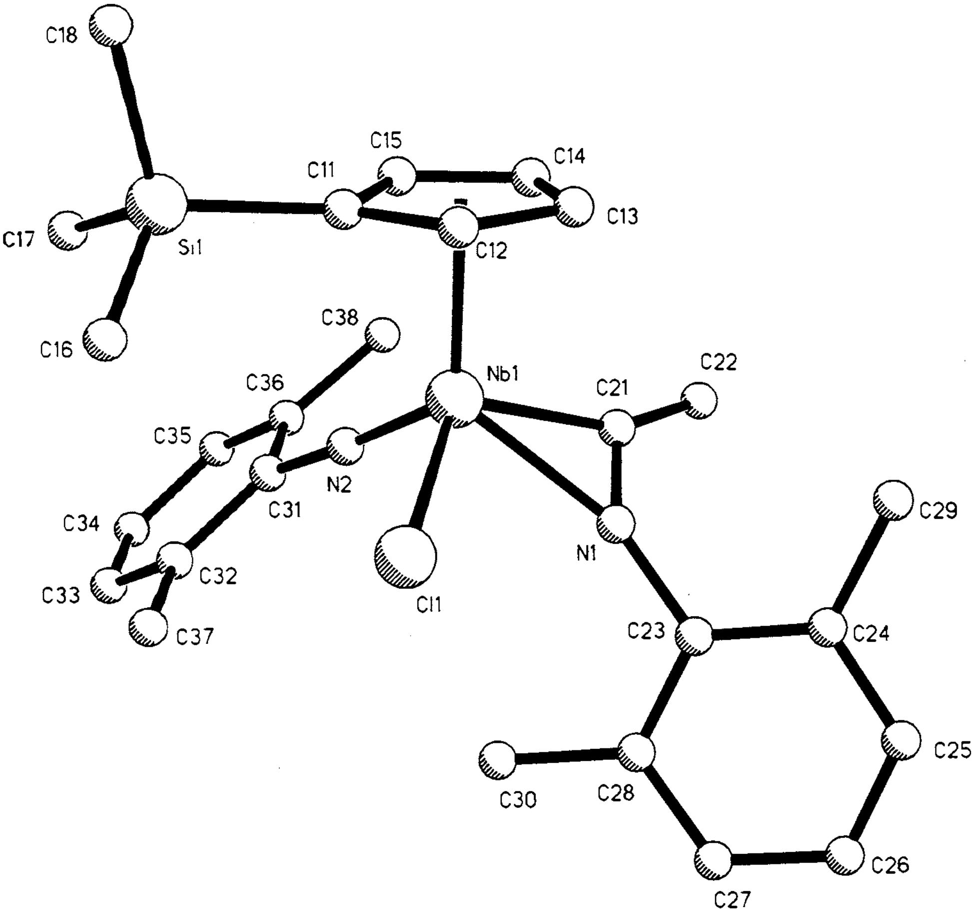


Fig. 1. Molecular structure and atom labelling scheme for complex [Nb(η^5-$C_5H_4SiMe_3$)Cl(NAr){η^2-C(Me)=NAr}] (Ar = 2,6-$Me_2C_6H_3$, **1**).

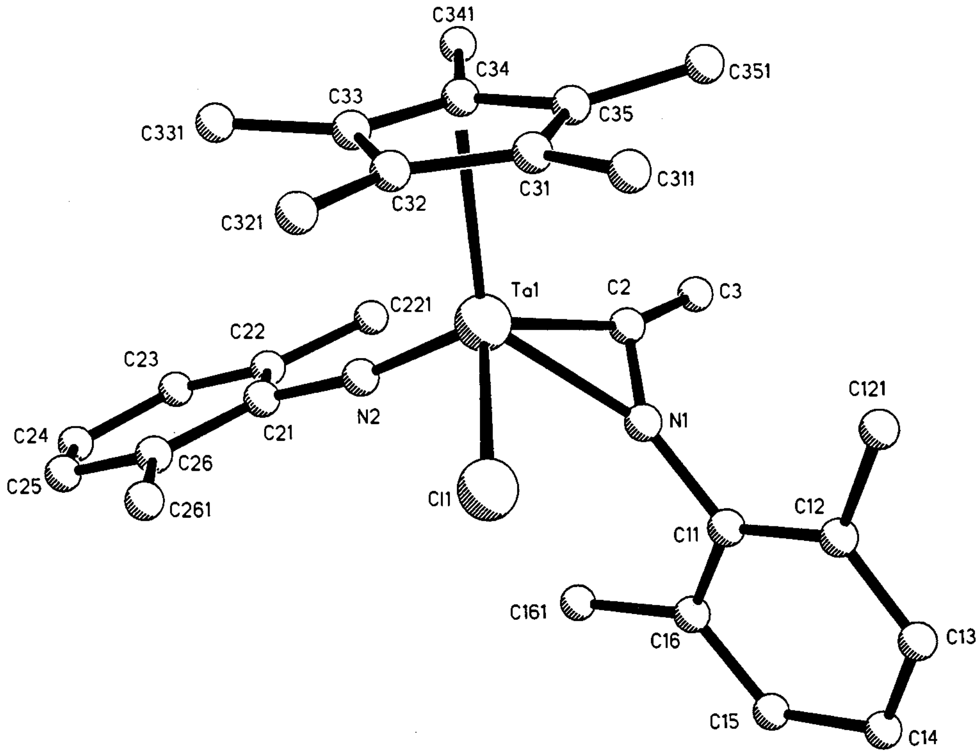


Fig. 2. Molecular structure and atom labelling scheme for complex [Ta(η^5-C_5Me_5)Cl(NAr){η^2-C(Me)=NAr}] (Ar = 2,6-$Me_2C_6H_3$, **7**).

1.273 for **7** [22] and their bond lengths and angles with the metal centres confirm the η^2-coordination.

2.2. Reactions with carbon monoxide

Dialkyl, alkyl chloro and alkyl methyl imido tantalum complexes [TaCp*XR(NAr)] react with carbon monoxide (1 atm) at r.t. in *n*-hexane or benzene-d_6 (NMR tube) to give alkyl η^2-acyl [TaCp*X(NAr){η^2-C(R)=O}] (Ar = 2,6-$Me_2C_6H_3$; X = R = CH_2SiMe_3, **31**; CH_2CMe_2Ph, **32**; CH_2CMe_3, **33**; CH_2Ph, **34**), chloro η^2-acyl and η^2-carbamoyl (X = Cl, R = CH_2CMe_2Ph, **35**; NMe_2, **36**) and methyl η^2-acyl (X = Me, R = CH_2CMe_2Ph, **37**; CH_2CMe_3, **38**) complexes, as result of simple migration of alkyl group bonded to the metal to the electrophilic carbonyl atom (Scheme 4), of the previously coordinated CO.

The regioselective synthesis of the methyl η^2-acyl complexes **37** and **38** reflects the preferential migration of CH_2CMe_2Ph and CH_2CMe_3 groups according with the sequence established for the isocyanide insertion process.

By this procedure, alkyl η^2-acyl derivatives with X = Cl, R = CH_2CMe_3; X = Me, R = 2-(CH_2NMe_2)C_6H_4 cannot be isolated or detected by ^{1}H-NMR spectroscopy probably due to their very low stability; however, dinuclear ene diolate complexes [{TaCp*X(NAr)}$_2$-{μ-η^2-OC(R)=C(R)O}] (Ar = 2,6-$Me_2C_6H_3$; X = Cl, R = CH_2CMe_3, **39**; X = Me, R = 2-(CH_2NMe_2)C_6H_4, **40**) are easily obtained when the corresponding chloro or methyl alkyl imido complex react with CO (1 atm) at r.t. in *n*-hexane (Scheme 5). This reaction takes place by intermolecular coupling between two acyl carbon atoms of the unstable intermediate η^2-acyl complexes '[TaCp*X(NAr){η^2-C(R)=O}]', which could not be observed when the reaction was followed by ^{1}H-NMR spectroscopy. However, for X = R = Me [5] we have observed the formation of the intermediate η^2-acyl complex [TaCp*Me(NAr){η^2-C(Me)=O}] when the reaction is followed by NMR spectroscopy at low temperature.

Table 3
Selected bond lengths (Å) and angles (°) for complex **1** [a]

Bond lengths			
Nb(1)–N(2)	1.781(2)	Nb(1)–C(21)	2.132(3)
Nb(1)–N(1)	2.166(2)	Nb(1)–Cl(1)	2.447(1)
N(1)–C(21)	1.265(3)	N(1)–C(23)	1.428(3)
N(2)–C(31)	1.394(3)	Nb(1)–Cp(1)	2.153
Bond angles			
N(2)–Nb(1)–C(21)	97.17(10)	N(2)–Nb(1)–N(1)	103.14(9)
N(2)–Nb(1)–Cl(1)	102.24(7)	C(21)–Nb(1)–Cl(1)	119.26(8)
N(1)–Nb(1)–Cl(1)	85.17(6)	C(21)–N(1)–C(23)	131.6(2)
C(21)–N(1)–Nb(1)	71.43(16)	C(23)–N(1)–Nb(1)	156.74(17)
C(31)–N(2)–Nb(1)	175.35(19)	N(1)–C(21)–C(22)	129.9(3)
C(22)–C(21)–Nb(1)	155.7(2)	Cp(1)–Nb(1)–Cl(1)	109.5
Cp(1)–Nb(1)–N(1)	126.6	Cp(1)–Nb(1)–N(2)	121.7
Cp(1)–Nb(1)–C(21)	107.4		

[a] Cp(1) is the centroid of the C(11)–C(15) cyclopentadienyl ring.

Table 4
Selected bond lengths (Å) and angles (°) for complex **7** [a]

Bond lengths			
Ta(1)–N(2)	1.795(6)	Ta(1)–C(2)	2.137(7)
Ta(1)–N(1)	2.139(6)	Ta(1)–Cl(1)	2.427(2)
N(1)–C(2)	1.273(9)	N(1)–C(11)	1.443(9)
N(2)–C(21)	1.382(11)	C(2)–C(3)	1.490(10)
Ta(1)–Cp*(1)	2.142		
Bond angles			
N(2)–Ta(1)–C(2)	99.5(3)	N(2)–Ta(1)–N(1)	104.3(3)
C(2)–Ta(1)–N(1)	34.7(2)	N(2)–Ta(1)–Cl(1)	102.6(2)
C(2)–Ta(1)–Cl(1)	118.2(2)	N(1)–Ta(1)–Cl(1)	83.90(17)
C(2)–N(1)–C(11)	131.8(6)	C(2)–N(1)–Ta(1)	72.6(4)
C(11)–N(1)–Ta(1)	155.0(5)	C(21)–N(2)–Ta(1)	170.2(6)
N(1)–C(2)–C(3)	126.5(7)	C(3)–C(2)–Ta(1)	160.6(6)
Cp*(1)–Ta(1)–N(1)	131.6	Cp*(1)–Ta(1)–N(2)	117.2
Cp*(1)–Ta(1)–Cl(1)	108.6	Cp*(1)–Ta(1)–C(2)	110.7

[a] Cp*(1) is the centroid of the C(31)–C(35) pentamethylcyclopentadienyl ring.

When the same reaction with CO was carried out using [TaCp*XR(NAr)] ($Ar = 2,6\text{-}Me_2C_6H_3$; X = Cl, $R = CH_2CMe_3$; X = R = Ph) as starting materials the expected imido η²-acyl derivatives were not obtained, since they were spontaneously converted into the oxo η²-iminoacyl complexes [TaCp*X(O){η²-C(R)=NAr}] after 35 days (X = Cl, $R = CH_2CMe_3$, **41**) and 12 h (X = R = Ph, **42**), respectively (Scheme 5). The formation of complexes **41**–**42** can be explained assuming three steps: (a) the initial formation of non-stable η²-acyl complex, (b) a nucleophilic attack of the imido nitrogen atom at the electrophilic acyl carbon atom leads to an unidentified intermediate and (c) spontaneous rearrangement, by the rupture of the C–O single bond and simultaneous formation of the Ta=O double bond to give the final oxo η²-iminoacyl complexes **41**–**42**, as we have proposed for similar methyl tantalum derivatives [5].

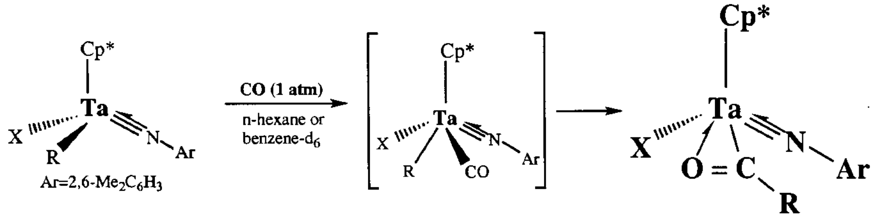
In the cases X = Cl, $R = CH_2SiMe_3$, CH_2Ph, Ph and X = Me, $R = CH_2SiMe_3$, CH_2Ph, Ph the reaction with CO takes place but leads to an unidentified mixture of products, whereas for X = Cl, $R = 2\text{-}(CH_2NMe_2)C_6H_4$ there is no reaction even on heating at 100°C.

All of the complexes **31**–**42** are soluble in aromatic and chlorinated solvents and partially soluble in saturated hydrocarbons.

The analytical (Section 3), IR (Table 1) and ¹H- and ¹³C{¹H}-NMR (Table 2) spectroscopic data for compounds **31**–**42** are consistent with their formulation. All the complexes show the characteristic absorption for the pentamethylcyclopentadienyl ring ($\nu_{C-C} \approx 1028$ cm^{-1}) [11]. The imido η²-acyl complexes **31**–**38** show the $\nu_{Ta=N}$ [15] and $\nu_{C(R)=O}$ [23] at ≈1327 and 1589 cm^{-1}, respectively. The C=O stretching vibration in η²-acyls ranges from 1453 to 1625 cm^{-1} and the lowest stretching frequencies occur for η²-acyl complexes containing high-valent metals, as in our case. This has been attributed to the participation of a 'carbene-like' resonance form [24] or to the contribution of a 'carbenium ion like' acceptor orbital on the undistorted η²-acyl structure [25].

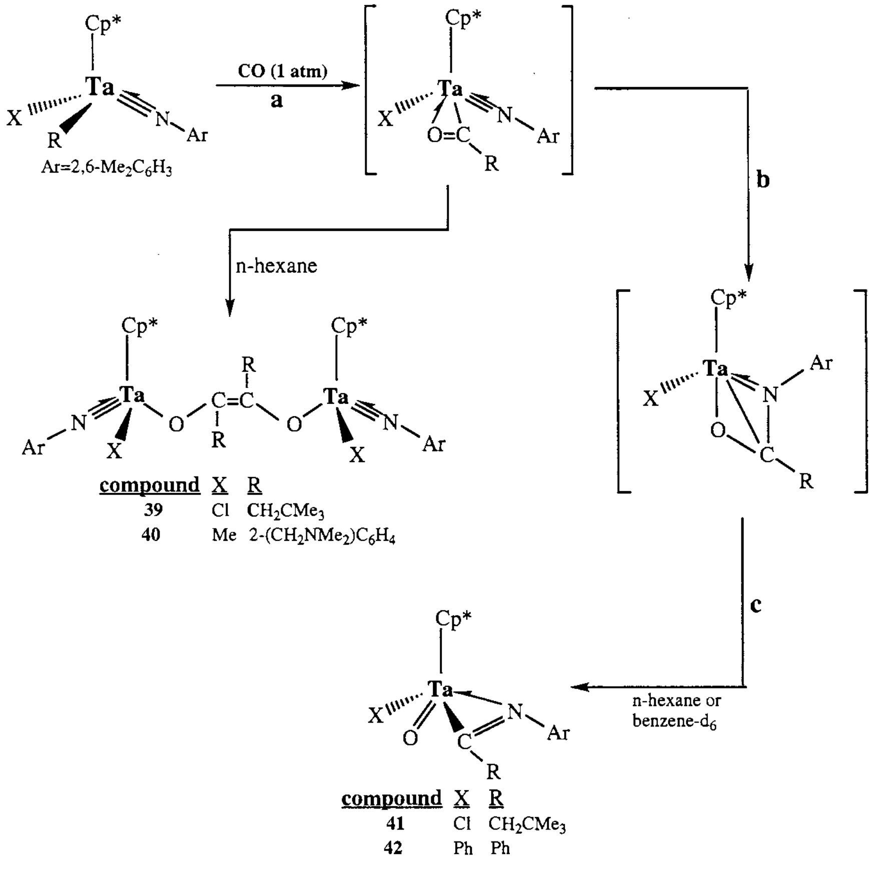
Their NMR data accord with the expected pseudo-square-pyramidal structure with chiral metal atoms. The η²-acyl carbon resonance appears at $\delta \approx 317$ but the corresponding to the η²-carbamoyl derivative **36** is shifted to higher field at δ 228, in the typical ranges for η²-acyl [26] and η²-carbamoyl [27] complexes. Further, the ¹H-NMR spectrum of the η²-carbamoyl complex **36** exhibits inequivalent methyl groups due to the slow rotation around the C_{acyl}–NMe_2 bond [10,18,27,28] like the organic amides.

The ene diolate complexes **39** and **40** show $\nu_{C=C}$ [2b,d, 29], $\nu_{Ta=N}$ [17], ν_{C-O} [29a] and ν_{Ta-O} [16a] IR absorptions at ≈1587, 1332, 1159 and 812 cm^{-1}, respectively, whereas the oxo η²-iminoacyl complexes **41** and **42** show the $\nu_{C(R)=N}$ [14] and $\nu_{Ta=O}$ [29c, 30] IR absorptions at 1601 and 901 cm^{-1}, respectively. In addition, its NMR spectra demonstrate all expected signals.



compound	X	R
31	CH_2SiMe_3	CH_2SiMe_3
32	CH_2CMe_2Ph	CH_2CMe_2Ph
33	CH_2CMe_3	CH_2CMe_3
34	CH_2Ph	CH_2Ph
35	Cl	CH_2CMe_2Ph
36		NMe_2
37	Me	CH_2CMe_2Ph
38		CH_2CMe_3

Scheme 4.



Scheme 5.

2.2.1. X-ray structure of [TaCp*Me(NAr)-{η^2-C(CH$_2$CMe$_2$Ph)=O}] (Ar = 2,6-Me$_2$C$_6$H$_3$, 37)

The molecular structure and atom-labelling scheme of **37** are shown in Fig. 3, while relevant geometrical parameters are summarised in Table 5. Compound **37** can be described as a monomer with the typical four-legged piano stool environment for the tantalum atom, where the four legs are occupied by the imido, methyl and the carbon and oxygen atoms of acyl group. Bond lengths and angles between the pentamethylcyclopentadienyl ring and the tantalum atom are in the normal range [2,5,21]. In relation with the imido disposition, the Ta(1)–N(1) [1.815(11) Å] bond distance is similar to that found in **7** and the Ta(1)–N(1)–C(21) [172.2(10)°] angle is in the range of linear imido ligands [4a,5].

On the other hand, the bonding system between the acyl group and the tantalum is very similar to that found in [TaCp*Cl$_3${η^2-C(CH$_2$CMe$_3$)=O}] [29c]. However, the Ta(1)–C(31) [2.126(14) Å] and Ta(1)–O(1) [2.214(11) Å] bond lengths are slightly longer than the corresponding in the trichloride derivative, due to the existing difference between the donor ability and *trans* effect of the chloride and imide ligands.

2.3. Concluding remarks

With this work we have completed a systematic study of the isocyanide and carbon monoxide insertion reactions into metal–carbon bonds of different alkyl imido cyclopentadienyl niobium and tantalum complexes. Stable 18-electron η^2-iminoacyl compounds [MCpX-(NAr){η^2-C(R)=NAr}] (**1**–**18**) are obtained by insertion of 2,6-Me$_2$C$_6$H$_3$NC into M–C(alkyl) bonds of alkyl chloro or dialkyl imido complexes MCpXR(NAr). In contrast, the reaction with alkyl methyl imido tantalum complexes takes place with migration of alkyl or methyl group to give mixture of methyl η^2-alkyliminoacyl [TaCp*Me(NAr){η^2-C(R)=NAr}] (**19**, **21**, **23**, **25**, **27**, **29**, **30**) and alkyl η^2-methyliminoacyl [TaCp*R-(NAr){η^2-C(Me)=NAr}] (**20**, **22**, **24**, **26**, **28**) derivatives, respectively. In the cases of the starting 2-[(dimethylamino)methyl]phenyl methyl and dimethylamido methyl imido complexes the insertion reactions take place with a regioselective migration of the 2-[(dimethylamino)methyl]phenyl and dimethylamido groups. Reactions of the alkyl imido tantalum(V) complexes with CO occur through the formation of the expected alkyl η^2-acyl (**31**–**34**), chloro η^2-acyl (**35**, **36**) and methyl η^2-acyl (**37**, **38**) [TaCp*X(NAr){η^2-

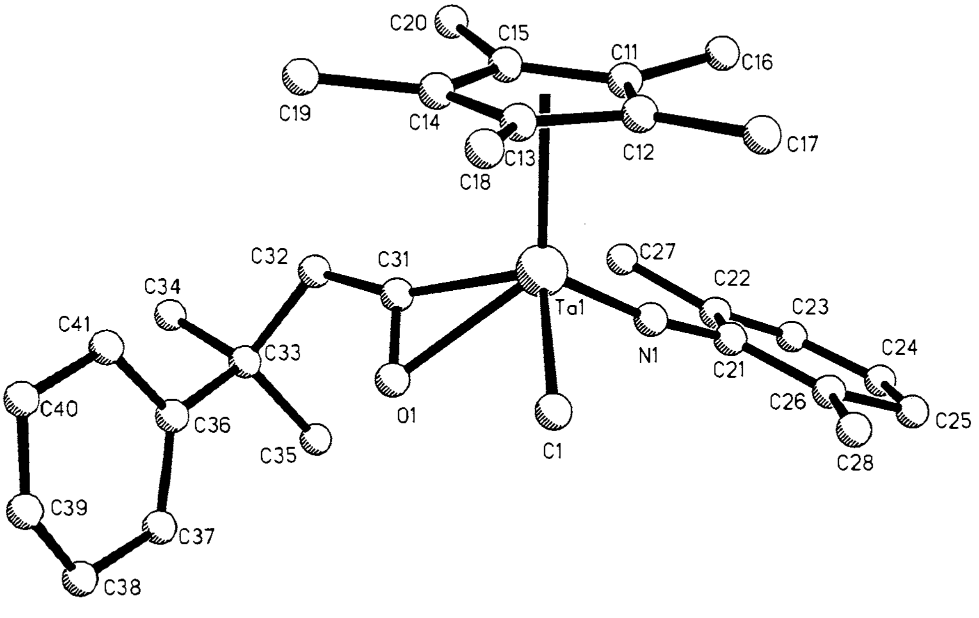


Fig. 3. Molecular structure and atom labelling scheme for complex [Ta(η^5-C_5Me_5)Me(NAr){η^2-C(CH_2CMe_2Ph)=O}] (Ar = 2,6-$Me_2C_6H_3$, **37**).

C(R)=O}] compounds, respectively, but lead to different products depending on X. The higher carbenoid character of the acyl ligand when X = Cl, R = CH_2CMe_3 and X = Me, R = 2-(CH_2NMe_2)C_6H_4, leads to the dinuclear ene diolate complexes [{TaCp*X-(NAr)}$_2${μ-η^2-OC(R) = C(R)O}] (**39**, **40**), whereas the nucleophilic attack of the imido nitrogen at the electrophilic acyl carbon atom when X = Cl, R = CH_2CMe_3 and X = R = Ph after long reaction times finally gives the oxo η^2-iminoacyl complexes [TaCp*X(O){η^2-C(R)=NAr}] (**41**, **42**).

3. Experimental

3.1. General considerations

All reactions and manipulations were carried out under an atmosphere of argon using standard Schlenk-tube and cannula techniques or in a conventional argon-filled glove-box. Solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use: chloroform-*d* (NaH), benzene-d_6 and *n*-hexane (Na–K alloy). Literature methods were employed for the synthesis of starting materials MCpXR(NAr) (Ar = 2,6-$Me_2C_6H_3$; M = Nb, Cp = η^5-$C_5H_4SiMe_3$ = Cp′, X = Cl, R = Me [4e]; X = Me, R = Me [4e], NMe_2 [4e]; M = Ta, Cp = η^5-C_5Me_5 = Cp*, X = Cl, R = Me [5], NMe_2 [4e], CH_2SiMe_3 [4d], CH_2CMe_2Ph [4d], CH_2CMe_3 [4d], $CH_2C_6H_5$ [4d], 2-(CH_2NMe_2)C_6H_4 [4d]; X = Me, R = NMe_2 [4e], CH_2SiMe_3 [4d], CH_2CMe_2Ph [4d], CH_2CMe_3 [4d], $CH_2C_6H_5$ [4d], C_6H_5 [4d], 2-(CH_2NMe_2)C_6H_4 [4d]; X = R = CH_2SiMe_3 [4d], CH_2CMe_2Ph [4d], CH_2CMe_3 [4d], $CH_2C_6H_5$ [4d], C_6H_5 [4d]). Reagents were purchased from commercial sources and used without further purification as follows: 2,6-$Me_2C_6H_3NC$ (Aldrich) and CO (Air Liquide).

Table 5
Selected bond lengths (Å) and angles (°) for complex **37** [a]

Bond lengths			
Ta(1)–N(1)	1.815(11)	Ta(1)–C(31)	2.126(14)
Ta(1)–O(1)	2.214(11)	Ta(1)–C(1)	2.220(14)
O(1)–C(31)	1.240(16)	C(31)–C(32)	1.490(19)
Ta(1)–Cp*(1)	2.124		
Bond angles			
N(1)–Ta(1)–C(31)	101.4(5)	N(1)–Ta(1)–O(1)	105.1(5)
C(31)–Ta(1)–O(1)	33.1(4)	N(1)–Ta(1)–C(1)	100.6(6)
C(31)–Ta(1)–C(1)	110.6(6)	O(1)–Ta(1)–C(1)	77.6(5)
C(21)–N(1)–Ta(1)	172.2(10)	O(1)–C(31)–C(32)	123.1(12)
O(1)–C(31)–Ta(1)	77.3(9)	C(32)–C(31)–Ta(1)	159.4(10)
Cp*(1)–Ta(1)–N(1)	121.2	Cp*(1)–Ta(1)–O(1)	128.7
Cp*(1)–Ta(1)–C(1)	111.3	Cp*(1)–Ta(1)–C(31)	110.9

[a] Cp*(1) is the centroid of the C(11)–C(15) pentamethylcyclopentadienyl ring.

Infrared spectra were recorded on a Perkin–Elmer 583 spectrophotometer (4000–200 cm^{-1}) as Nujol mulls between CsI or polyethylene pellets. ^1H- and $^{13}C\{^1H\}$-NMR spectra were recorded on Varian Unity 300 and Varian Unity 500 Plus spectrometers and chemical shifts were measured relative to residual ^1H and ^{13}C resonances in the deuterated solvents C_6D_6(δ 7.15), $CDCl_3$(δ 7.24) and C_6D_6(δ 128), $CDCl_3$(δ 77), respectively. C, H and N analyses were carried out with a Perkin–Elmer 240C microanalyzer.

3.2. Synthesis of [NbCp′X{N(2,6-Me$_2$C$_6$H$_3$)}-{η^2-C(R)=N(2,6-Me$_2$C$_6$H$_3$)}] (X = Cl, R = Me, ***1****; X = Me, R = NMe$_2$,* ***2****; Me,* ***3****; X = R = CH$_2$SiMe$_3$,* ***4****; CH$_2$CMe$_3$,* ***5****; CH$_2$Ph,* ***6****)*

A solution of CN(2,6-Me$_2$C$_6$H$_3$) (**1**, 0.23 g, 1.75 mmol; **2**, 0.22 g, 1.72 mmol; **3**, 0.24 g, 1.84 mmol; **4**, 0.17 g, 1.33 mmol; **5**, 0.19 g, 1.42 mmol; **6**, 0.17 g, 1.32 mmol) in *n*-hexane (15 ml) was added at r.t. to a solution of [NbCp′XR{N(2,6-Me$_2$C$_6$H$_3$)}] (0.70 g; **1**, 1.75 mmol; **2**, 1.72 mmol; **3**, 1.84 mmol; **4**, 1.33 mmol; **5**, 1.42 mmol; **6**, 1.32 mmol) in *n*-hexane (25 ml) and the mixture was stirred for 12 h. **1** and **6** can be separated as insoluble pale-yellow (**1**) and brown (**6**) microcrystalline solids, whereas in the other cases, the resulting solution was filtered, concentrated to ca. 10 ml and cooled to −40°C to give the η^2-iminoacyl derivates as brown (**2**, **4**, **5**) and orange(**3**) crystals.

The data for **1** follow. Yield 0.70 g (85%). Anal. Found: C, 59.13; H, 6.50; N, 5.19. $C_{26}H_{34}ClN_2SiNb$. Calc.: C, 58.83; H, 6.41; N, 5.28%.

The data for **2** follow. Yield 0.39 g (42%). Anal. Found: C, 62.11; H, 7.40; N, 7.78. $C_{28}H_{40}N_3SiNb$. Calc.: C, 62.35; H, 7.42; N, 7.68%.

The data for **3** follow. Yield 0.65 g (70%). Anal. Found: C, 63.41; H, 7.25; H, 5.47. $C_{27}H_{37}N_2SiNb$. Calc.: C, 63.51; H, 7.30; N, 5.49%.

Tha data for **4** follow. Yield 0.65 g (75%). Anal. Found: C, 59.71; H, 8.25; N, 4.29. $C_{32}H_{53}N_2Si_3Nb$. Calc.: C, 59.78; H, 8.31; N, 4.36%.

The data for **5** follow. Yield 0.66 g (75%). Anal. Found: C, 66.76; H, 8.69; N, 5.02. $C_{34}H_{53}N_2SiNb$. Calc.: C, 66.86; H, 8.75; N, 4.59%.

The data for **6** follow. Yield 0.76 g (85%). Anal. Found: C, 69.84; H, 6.90; N, 4.27. $C_{39}H_{45}N_2SiNb$. Calc.: C, 70.70; H, 6.80; N, 4.23%.

*3.3. Synthesis of [TaCp*Cl(NAr){η^2-C(R)=NAr}] (Ar = 2,6-Me$_2$C$_6$H$_3$; R = CH$_2$SiMe$_3$,* ***8****; CH$_2$CMe$_2$Ph,* ***9****; CH$_2$CMe$_3$,* ***10****; CH$_2$C$_6$H$_5$,* ***11****; 2-(CH$_2$NMe$_2$)C$_6$H$_4$,* ***12****; NMe$_2$,* ***13****)*

A sample of [TaCp*ClR(NAr)] (0.50 g; R = CH$_2$SiMe$_3$, 0.76 mmol; CH$_2$CMe$_2$Ph, 0.82 mmol; CH$_2$CMe$_3$, 0.92 mmol; CH$_2$C$_6$H$_5$, 0.89 mmol; 2-(CH$_2$NMe$_2$)C$_6$H$_4$, 0.82 mmol; NMe$_2$, 0.97 mmol) was dissolved in 25 ml of *n*-hexane in a Schlenk tube. After addition of a *n*-hexane (10 ml) solution of isocyanide ArNC (R = CH$_2$SiMe$_3$, 0.10 g, 0.76 mmol; CH$_2$CMe$_2$Ph, 0.11 g, 0.82 mmol; CH$_2$CMe$_3$, 0.12 g, 0.92 mmol; CH$_2$C$_6$H$_5$, 0.116 g, 0.89 mmol; 2-(CH$_2$NMe$_2$)C$_6$H$_4$, 0.11 g, 0.82 mmol; NMe$_2$, 0.127 g, 0.97 mmol) the colour of the mixture changed quickly to yellow. The reaction mixture was stirred for 6 h at r.t. and then the resulting suspension was decanted and filtered. The residual solid was washed with cold *n*-hexane (2 × 5 ml), dried in vacuo and identified as complexes **8**–**10**, **12** (yellow), **11** (pale brown) and **13** (pale yellow). The filtrate was concentrated to ca. 10 ml and cooled to −40°C to give **8**–**13** as microcrystalline solids.

The data for **8** follow. Yield 0.40 g (80%). Anal. Found: C, 56.18; H, 6.46; N, 4.20. $C_{31}H_{44}ClN_2SiTa$. Cal.: C, 56.31; H, 6.71; N, 4.24%.

The data for **9** follow. Yield 0.48 g (80%). Anal. Found: C, 60.39; H, 6.45; N, 3.98. $C_{37}H_{46}ClN_2Ta$. Calc.: C, 60.45; H, 6.30; N, 3.81%.

The data for **10** follow. Yield 0.49 g (80%). Anal. Found: C, 56.93; H, 6.55; N, 4.23. $C_{32}H_{44}ClN_2Ta$. Calc.: C, 57.10; H, 6.59; N, 4.16%.

The data for **11** follow. Yield 0.49 g (80%). Anal. Found: C, 58.45; H, 5.95; N, 4.12. $C_{34}H_{40}ClN_2Ta$. Calc.: C, 58.92; H, 5.82; N, 4.04%.

The data for **12** follow. Yield 0.39 g (80%). Anal. Found: C, 58.89; H, 5.81; N, 5.71. $C_{36}H_{45}ClN_3Ta$. Calc.: C, 58.77; H, 6.16; N, 5.71%.

The data for **13** follow. Yield 0.50 g (80%). Anal. Found: C, 53.86; H, 6.18; N, 6.47. $C_{29}H_{39}ClN_3Ta$. Calc.: C, 53.91; H, 6.08; N, 6.50%.

*3.4. Synthesis of [TaCp*R(NAr){η^2-C(R)=NAr}] (Ar = 2,6-Me$_2$C$_6$H$_3$; R = CH$_2$SiMe$_3$,* ***14****; CH$_2$-CMe$_2$Ph,* ***15****; CH$_2$CMe$_3$,* ***16****; CH$_2$C$_6$H$_5$,* ***17****; C$_6$H$_5$,* ***18****)*

A stirred solution of [TaCp*R$_2$(NAr)] (0.50 g; R = CH$_2$SiMe$_3$, 0.82 mmol; CH$_2$CMe$_2$Ph, 0.71 mmol; CH$_2$CMe$_3$, 0.86 mmol; CH$_2$C$_6$H$_5$, 0.81 mmol; C$_6$H$_5$, 0.77 mmol), in *n*-hexane (30 ml) was treated with ArNC (R = CH$_2$SiMe$_3$, 0.107 g; CH$_2$CMe$_2$Ph, 0.09 g; CH$_2$CMe$_3$, 0.11 g; CH$_2$C$_6$H$_5$, 0.106 g; C$_6$H$_5$, 0.109 g) in a 1:1 molar ratio and under rigorously anhydrous conditions for 6 h. Complexes **14**–**18** were obtained as precipitates and then separated by filtration. The solution was concentrated to ca. 10 ml and cooled to −40°C to give **14**, **15** (pale brown), **16**, **17** (yellow) and **18** (orange) microcrystalline solids.

The data for **14** follow. Yield 0.48 g (80%). Anal. Found: C, 56.65; H, 7.38; N, 3.71. $C_{35}H_{55}N_2Si_2Ta$. Calc.: C, 56.73; H, 7.48; N, 3.78%.

The data for **15** follow. 0.47 g (80%). Anal. Found: C, 67.68; H, 7.04; N, 3.26. $C_{47}H_{59}N_2Ta$. Calc.: C, 67.77; H, 7.14; N, 3.36%.

The data for **16** follow. Yield 0.49 g (80%). Anal. Found: C, 62.60; H, 7.74; N, 3.84. $C_{37}H_{55}N_2Ta$. Calc.: C, 62.70; H, 7.82; N, 3.95%.

The data for **17** follow. Yield 0.48 g (80%). Anal. Found: C, 65.63; H, 6.22; N, 3.62. $C_{41}H_{47}N_2Ta$. Calc.: C, 65.76; H, 6.32; N, 3.74%.

The data for **18** follow. Yield 0.44 g (80%). Anal. Found: C, 65.24; H, 5.94; N, 4.02. $C_{39}H_{43}N_2Ta$. Calc.: C, 65.00; H, 6.01; N, 3.89%.

3.5. Synthesis of [TaCp*Me(NAr){η^2-C(R)=NAr}] and [TaCp*R(NAr){η^2-C(Me)=NAr}] (Ar = 2,6-$Me_2C_6H_3$; R = CH_2SiMe_3, **19**; $CH_2C_6H_5$, **21** and R = CH_2SiMe_3, **20**; $CH_2C_6H_5$, **22**)

3.5.1. Method A

A solution of isocyanide 2.6-$Me_2C_6H_3NC$ (0.12 g, 0.92 mmol) in *n*-hexane (15 ml) was added at r.t. to a yellow solution of [TaCp*RMe(NAr)] (0.50 g; R = CH_2SiMe_3, 0.93 mmol; $CH_2C_6H_5$, 0.923 mmol) in *n*-hexane (25 ml) and stirred for 6 h. The resulting yellow suspension was decanted, filtered, the yellow microcrystalline solids washed twice with cold *n*-hexane (2 × 5 ml) and identified as **20** and **22**.

The data for **20** follow. Yield 0.43 g (70%). Anal. Found: C, 57.57; H, 6.89; N, 3.09. $C_{32}H_{47}N_2SiTa$. Calc.: C, 57.47; H, 7.08; H, 4.19%.

The data for **22** follow. Yield 0.49 g (80%). Anal. Found: C, 62.29; H, 6.60; N, 4.09. $C_{47}H_{43}N_2Ta$. Calc.: C, 62.49; H, 6.44; N, 4.16%.

3.5.2. Method B

In a typical experiment [TaCp*RMe(NAr)] (0.25 g; R = CH_2SiMe_3, 0.465 mmol; $CH_2C_6H_5$, 0.4612 mmol), ArNC (0.06 g, 0.46 mmol) and benzene-d_6 (0.7 ml) were placed in a valved NMR tube. The reaction was monitored by ^{1}H-NMR spectroscopy until the starting material was totally transformed and no further change was observed. The formation of the corresponding η^2-iminoacyl complexes **19**–**22** was confirmed by their ^{1}H-NMR spectrum. Yield: R = CH_2SiMe_3, **19**, 30%; **20**, 70%; $CH_2C_6H_5$, **21**, 20%; **22**, 80%.

When the yellow suspension obtained by method A was evaporated to dryness, a ^{1}H-NMR spectrum in benzene-d_6 of the crude residue gave the same result.

3.6. Synthesis of [TaCp*Me(NAr){η^2-C(R)=NAr}] and [TaCp*R(NAr){η^2-C(Me)=NAr}] (Ar = 2,6-$Me_2C_6H_3$, R = CH_2CMe_2Ph, **23**; CH_2CMe_3, **25**; C_6H_5, **27**; 2-(CH_2NMe_2)C_6H_4, **29**; NMe_2, **30** and R = CH_2CMe_2Ph, **24**; CH_2CMe_3, **26**; C_6H_5, **28**)

3.6.1. Method A

The mixed alkyl imido complex [TaCp*RMe(NAr)] (0.50 g; R = CH_2CMe_2Ph, 0.85 mmol; CH_2CMe_3, 0.96 mmol; C_6H_5, 0.94 mmol; 2-(CH_2NMe_2)C_6H_4, 0.85 mmol; NMe_2, 1 mmol) was dissolved in 25 ml of *n*-hexane and isocyanide 2,6-$Me_2C_6H_3NC$ (R = CH_2CMe_2Ph, 0.11 g; CH_2CMe_3, 0.126 g; C_6H_5, 0.123 g; 2-(CH_2NMe_2)C_6H_4, 0.11 g; NMe_2, 0.13 g) in an 1:1 molar ratio was added. The solution was stirred and the yellow (**23**, **25**, **27**, **29**) or beige (**30**) microcrystalline solids formed after 6 h, were collected by decanting the solvent and washing with 5 ml of cold *n*-hexane.

The data for **23** follow. Yield 0.45 g (75%). Anal. Found: C, 63.71; H, 7.03; N, 3.88. $C_{38}H_{49}N_2Ta$. Calc.: C, 63.86; H, 6.91; N, 3.92%.

The data for **25** follow. Yield 0.48 g (77%). Anal. Found: C, 60.68; H, 7.21; N, 4.32. $C_{33}H_{47}N_2Ta$. Calc.: C, 60.73; H, 7.26; N, 4.29%.

The data for **27** follow. Yield 0.43 g (70%). Anal. Found: C, 61.96; H, 6.22; N, 4.35. $C_{34}H_{41}N_2Ta$. Calc.: C, 62.00; H, 6.27; N, 4.25%.

The data for **29** follow. Yield 0.54 g (90%). Anal. Found: C, 61.82; H, 6.86; N, 5.88. $C_{37}H_{48}N_3Ta$. Calc.: C, 62.09; H, 6.76; N, 5.87%.

The data for **30** follow. Yield 0.53 g (85%). Anal. Found: C, 57.49; H, 6.59; N, 6.66. $C_{30}H_{42}N_3Ta$. Calc.: C, 57.59; H, 6.76; N, 6.71%.

3.6.2. Method B

In a standard experiment, a solution of [TaCp*RMe(NAr)] (0.25 g; R = CH_2CMe_2Ph, 0.425 mmol; CH_2CMe_3, 0.48 mmol; C_6H_5, 0.47 mmol; 2-(CH_2NMe_2)C_6H_4, 0.425 mmol; NMe_2, 0.5 mmol) in 0.8 ml of benzene-d_6 was prepared and transfered to a valved NMR tube containing an equimolar amount of isocyanide 2,6-$Me_2C_6H_3NC$ (R = CH_2CMe_2Ph, 0.055g; CH_2CMe_3, 0.063 g; C_6H_5, 0.0615 g; 2-(CH_2NMe_2)C_6H_4, 0.055 g; NMe_2, 0.065 g). The solution was shaken until homogeneous and the reaction monitored by ^{1}H-NMR spectroscopy until total conversion of the tantalum starting complex to the η^2-iminoacyl complexes **23**–**30**. The yield was determined from sealed NMR tube reactions; R = CH_2CMe_2Ph, **23**, 75%; **24**, 25%; CH_2CMe_3, **25**, 77%; **26**, 23%; C_6H_5, **27**, 70%; **28**, 30%; 2-(CH_2NMe_2)C_6H_4, **29**, 100%; NMe_2, **30**, 100%.

When the yellow suspension obtained by method A was evaporated to dryness, a ^{1}H-NMR spectrum in benzene-d_6 of the crude residue gave the same result.

3.7. Synthesis of [TaCp*X(NAr){η^2-C(R)=O}] (Ar = 2,6-$Me_2C_6H_3$; X = R = CH_2SiMe_3, **31**; CH_2CMe_2Ph, **32**; CH_2CMe_3, **33**; CH_2Ph, **34**)

3.7.1. Method A

An *n*-hexane (35 ml) solution of [TaCp*XR(NAr)] (0.50 g; X = R = CH_2SiMe_3, 0.82 mmol; CH_2CMe_2Ph, 0.71 mmol; CH_2CMe_3, 0.86 mmol) was placed into a Schlenk tube under a CO atmosphere (1 atm) and the mixture then was stirred at r.t. for 12 (X = R = CH_2SiMe_3), 24 (X = R = CH_2CMe_2Ph) and 72 (X = R = CH_2CMe_3) h. The resulting suspension was evaporated to dryness and the residue extracted into *n*-hexane (2 × 15 ml). The solution was filtered, concentrated to ca. 10 ml and cooled to −40°C to give **31**–**33** as deep-yellow (**31**), pale-brown (**32**) and brown (**33**) microcrystalline solids.

The data for **31** follow. Yield 0.35 g (75%). Anal. Found: C, 55.56; H, 7.77; N, 2.28. $C_{27}H_{46}ONSi_2Ta$. Calc.: C, 55.76; H, 7.97; N, 2.41%.

The data for **32** follow. Yield 0.36 g (70%). Anal. Found: C, 64.05; H, 6.86; N, 1.86. $C_{39}H_{50}ONTa$. Calc.: C, 64.18; H, 6.90; N, 1.92%.

The data for **33** follow. Yield 0.36 g (70%). Anal. Found: C, 57.41; H, 7.59; N, 2.27. $C_{29}H_{46}ONTa$. Calc.: C, 57.51; H, 7.65; N, 2.31%.

3.7.2. Method B

A benzene-d_6 (0.6 ml) solution of [TaCp*XR(NAr)] (X = R = CH_2Ph, 0.125 g, 0.20 mmol) was placed in a NMR tube under a CO atmosphere (1 atm) and then the tube flame sealed. The yellow colour of the mixture no changed, but the reaction was instantaneous and monitored by ^{1}H-NMR spectroscopy confirmed the complete conversion of the dibenzyl imido complex into **34**.

*3.8. Synthesis of [TaCp*X(NAr){η^2-C(R)=O}] (Ar = 2,6-$Me_2C_6H_3$; X = Cl, R = CH_2CMe_2Ph, **35**; NMe_2, **36**; X = Me, R = CH_2CMe_2Ph, **37**; CH_2CMe_3, **38**)*

3.8.1. Method A

A solution of [TaCp*XR(NAr)] (0.50 g, X = Cl, R = CH_2CMe_2Ph, 0.71 mmol; X = Me, R = CH_2CMe_2Ph, 0.85 mmol; CH_2CMe_3, 0.96 mmol) in *n*-hexane (35 ml) was placed in an ampoule under a CO atmosphere (1 atm) and then sealed. The reaction mixture was stirred at r.t. for 12 h. After the ampoule was opened, the suspension evaporated to dryness and the residue recrystallized from *n*-hexane at −40°C to give **35**, **37** and **38** as yellow microcrystalline solids.

The data for **35** follow. Yield 0.33 g (75%). Anal. Found: C, 55.05; H, 5.92; N, 2.19. $C_{29}H_{37}OClNTa$. Calc.: C, 55.11; H, 5.90; N, 2.22%.

The data for **37** follow. Yield 0.39 g (75%). Anal. Found: C, 58.92; H, 6.22; N, 2.26. $C_{30}H_{40}ONTa$. Calc.: C, 58.91; H, 6.59; N, 2.29%.

The data for **38** follow. Yield 0.39 g (75%). Anal. Found: C, 54.47; H, 6.89; N, 2.47. $C_{25}H_{38}ONTa$. Calc.: C, 54.64; H, 6.97; N, 2.55%.

3.8.2. Method B

In a typical experiment, a $CDCl_3$ (0.7 ml) solution of [TaCp*Cl(NMe_2)(NAr)] (0.125 g, 0.24 mmol) was placed into a NMR tube, the argon atmosphere replaced by CO and the tube flame sealed. The disappearance of starting tantalum complex and formation of **36** were monitored as the reaction progressed at 25°C.

*3.9. Synthesis of [{TaCp*X(NAr)}$_2${μ-η^2-OC(R)=C(R)O}] (Ar = 2,6-$Me_2C_6H_3$; X = Cl, R = CH_2CMe_3, **39**; X = Me, R = 2-(CH_2NMe_2)C_6H_4, **40**)*

A yellow solution of [TaCp*XR(NAr)] (0.50 g; X = Cl, R = CH_2CMe_3, 0.86 mmol; X = Me, R = 2-(CH_2NMe_2)C_6H_4, 0.85 mmol) in *n*-hexane (35 ml) was charged into a Schlenk tube under rigorously anhydrous conditions. The argon atmosphere was replaced by CO (1 atm) and the solution stirred for 12 h. From the resulting yellow suspension microcrystalline solids were collected by filtration, dried in vacuo and identified as **39** and **40**.

The data for **39** follow. Yield 0.39 g (80%). Anal. Found: C, 50.47; H, 6.21; N, 2.48. $C_{48}H_{70}O_2Cl_2N_2Ta$. Calc.: C, 50.58; H, 6.19; N, 2.46%.

The data for **40** follow. Yield 0.41 g (80%). Anal. Found: C, 56.71; H, 6.53; N, 4.47. $C_{58}H_{78}O_2N_4Ta$. Calc.: C, 56.86; H, 6.42; N, 4.57%.

*3.10. Synthesis of [TaCp*Cl(O){η^2-C(CH_2CMe_3)=NAr}] (Ar = 2,6-$Me_2C_6H_3$, **41**)*

In a NMR tube, a benzene-d_6 (0.7 ml) solution of [TaCp*Cl(CH_2CMe_3)(NAr)] (0.16 g, 0.28 mmol) was placed and the argon atmosphere replaced by CO (1 atm). The NMR tube was sealed and the reaction monitored by NMR spectroscopy at r.t. After 35 days the formation of the corresponding chloro oxo η^2-iminoacyl complex **41** was confirmed by their ^{1}H- and ^{13}C-NMR spectra.

*3.11. Synthesis of [TaCp*Ph(O){η^2-C(Ph) = NAr}] (Ar = 2,6-$Me_2C_6H_3$, **42**)*

A red–orange solution of [TaCp*Ph_2(NAr)] (0.48 g, 0.74 mmol) in *n*-hexane (40 ml) was placed into a Schlenk tube and the argon atmosphere replaced by carbon monoxide (1 atm). The reaction mixture was stirred at r.t. for 12 h and then, the resulting suspension evaporated to dryness. The residue was recrystallized from *n*-hexane to give **42** as a yellow microcrystalline solid.

The data for **42** follow. Yield 0.35 g (75%). Anal. Found: C, 60.22; H, 5.48; N, 2.29. $C_{31}H_{34}ONTa$. Calc.: C, 60.29; H, 5.55; N, 2.26%.

*3.12. X-ray structure determination of compounds **1**, **7** and **37***

Table 6 provides a summary of the crystal data, data collection and refinement parameters for complexes **1**, **7** and **37**. All data were collected on an Enraf Nonius CAD4 diffractometer at r.t. Intensity measurements were performed by ω scans in the range $6° < 2\theta < 50°$ for **1**, $\omega - 2\theta$ $4° < 2\theta < 50°$ for **7** and $\omega - \theta$ $6° < 2\theta < 50°$ for **37**. Of the 5363 measured reflections for **1**, 4699 were independent; $R_1 = 0.029$ and $wR_2 = 0.073$ (for 3846 reflections with $F > 4\sigma(F)$). Of the 5059 measured reflections for **7**, 4758 were independent; $R_1 = 0.037$ and $wR_2 = 0.100$ (for 3740 reflections with $F > 4\sigma(F)$). A total of 4910 independent reflections were measured for **37**, $R_1 = 0.080$ and $wR_2 = 0.171$ (for 2557 reflections

Table 6
Crystal data and structure refinement for complexes **1**, **7** and **37** [a]

	1	**7**	**37**
Empirical formula	$C_{26}H_{34}ClN_2NbSi$	$C_{28}H_{36}ClN_2Ta$	$C_{30}H_{40}NOTa$
M	531.00	616.99	611.58
Crystal system; space group	Monoclinic; $P2_1/n$	Monoclinic; $P2_1/n$	Orthorhombic; $Pbca$
a, b, c (Å)	10.292(3), 15.333(1), 17.256(4)	9.341(3), 24.653(4), 12.055(3)	15.070(6), 15.859(2), 23.464(4)
β (°)	100.40(1)	103.40(1)	
U (Å^3)	2678.4(10)	2700.5(12)	5608(3)
Z	4	4	8
D_{calc} (g cm^{-3})	1.317	1.518	1.449
μ(Mo–K$_\alpha$) (mm^{-1})	0.609	4.186	3.941
F(000)	1104	1232	2464
Crystal size (mm)	$0.48 \times 0.44 \times 0.38$	$0.48 \times 0.45 \times 0.38$	$0.38 \times 0.34 \times 0.27$
θ range for data collection (°)	3.14–25.03	2.39–25.16	3.03–25.03
Index ranges	$0<h<12$, $0<k<18$, $-20<l<20$	$0<h<11$, $0<k<29$, $-14<l<13$	$-17<h<0$, $0<k<18$, $-27<l<0$
Reflections collected	5363	5059	4910
Independent reflections	4699 [$R_{int} = 0.0222$]	4758 [$R_{int} = 0.0277$]	4910 [$R_{int} = 0.001$]
Observed reflections [$I>2\sigma(I)$]	3846		2557
Absorption correction	Psi scan	Psi scan	Psi scan
Max. and min. transmission	0.317 and 0.291	0.349 and 0.268	1.000 and 0.000
Data/restraints/parameters	4699/0/288	4758/0/289	4910/0/298
Goodness–of–fit on F^2	1.046	1.172	0.926
Final R_1, wR_2 indices [$I>2\sigma(I)$]	0.029, 0.073	0.037, 0.099	0.080, 0.171
(all data)	0.045, 0.078	0.064, 0.120	0.151, 0.191
Weighting scheme, w	$1/[\sigma^2(F_o^2)+(0.0359P)^2+1.4953P]$	$1/[\sigma^2(F_o^2)+(0.0636P)^2+5.5060P]$	$1/[\sigma^2(F_o^2)+(0.1173P)^2]$
Largest diff. peak, hole (e Å^{-3})	0.308, −0.287	1.885, −2.263	1.720, −1.724

[a] Details in common: Mo–K$_\alpha$ radiation (10.71073 Å); $P = (F_o^2 + 2F_c^2)/3$.

with $F > 4\sigma(F)$). The values of R_1 and wR_2 are defined $R_1 = \Sigma\, ||F_o| - |F_c||[\Sigma\, |F_o|]$; $wR_2 = \{[\Sigma\, w(F_o^2 - F_c^2)^2]/[\Sigma\, w(F_o)^2]\}^{1/2}$. The structures were solved by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97) [31].

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 130870 for **1**, 130869 for **7** and 130868 for **37**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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