Synthesis of 2

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CNXylyl)(PHPh_2)]Cl$ (**1**) (0.62 g, 0.87 mmol) in toluene (30 mL) was treated with 0.5 M aqueous NaOH (1.72 mL, 10% excess). The mixture was vigorously stirred. Within 4 h the precipitate had dissolved and the organic phase turned dark brown. The toluene solution was filtered and evaporated to dryness. Complex **2** was obtained as a yellow-brown oily material.

(**2**) Yield = 80%**.** IR (Nujol): ν (cm^{-1}) 1990 (C≡N). ^{1}H NMR (500 MHz, C_6D_6): δ 0.08 (s, 18 H, Si*Me*$_3$), 2.05 (s, 6 H, C*H*$_3$, CNXylyl), 4.58, 4.86, 4.98, 5.1 (m, 2 H each complex signal, $C_5H_4SiMe_3$), 6.95, 6.77, 6.91, 7.59 (m, C_6H_5). ^{13}C{H} NMR (125 MHz, C_6D_6): δ 0.5 (Si*Me*$_3$), 97.3 (*C*^{1}, $C_5H_4SiMe_3$), 93.2, 97.5, 100.9, 103.4 (*C*$^{2\text{-}5}$, exact assignment not possible, $C_5H_4SiMe_3$), 124.8, 126.2, 134.0 (*C*$_6$H$_5$), 133.0 (d, $^2J_{C\text{-}P}$ = 15.70 Hz, C_6H_5), 152.3 (d, $^1J_{C\text{-}P}$ = 30.00 Hz, C_6H_5), 217.2 (*C*NXylyl). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ –0.3 (*P*Ph$_2$). Anal. Calcd for $C_{37}H_{45}NNbPSi_2$: C, 62.08; H, 6.34; N, 1.96. Found: C, 61.85; H, 6.78; N, 2.15.

Syntheses of 3 and 4

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CNXylyl)(PPh_2)]$ (**2**) (0.60 g, 0.75 mmol) in thf (30 mL) was treated with methyl propiolate (0.07 g, ρ = 0.94 gL^{-1}, 0.75 mmol) at 0ºC (ice bath) with vigorous stirring for 10 min. The thf solution was filtered and the solvent evaporated to dryness. Complex **3** was obtained as a deep-red solid after washing with hexane (5 mL) at 0 ºC. Complex **4** was prepared using a similar method to complex **3** but using methyl butynoate.

(3) Yield = 85%**.** IR (Nujol): ν (cm^{-1}) 1718 (COO), 1630 (C=N), 1583 (C=C). ^{1}H NMR (500 MHz, C_6D_6): δ 0.22 (s, 18 H, Si*Me*$_3$), 2.32 (s, 6 H, C*H*$_3$, CNXylyl), 3.07 (s, 3H, C=CCO$_2$C*H*$_3$), 4.42 (m, 2 H complex signal, $C_5H_4SiMe_3$), 4.74 (m, 4 H complex signal, $C_5H_4SiMe_3$), 5.38 (m, 2 H complex signal, $C_5H_4SiMe_3$), 6.91 (m, 9H, *Ph*), 7.52 (t, 4 H, $^3J_{HH}$ = 8.06 Hz, P*Ph*$_2$); 7.62 (d, 1 H, $^2J_{HP}$ = 2.44 Hz, *H*C=C). ^{13}C{H} NMR (125 MHz, C_6D_6): δ 0.4 (Si*Me*$_3$), 20.0 (*C*H$_3$, CNXylyl), 51.2 (C=CCO$_2$*C*H$_3$), 98.3 (C^1), 87.1, 95.5, 98.2, 106.5 (C$^{2\text{-}5}$, exact assignment not possible, $C_5H_4SiMe_3$), 121.4–129.3 (*C*$_6$H$_5$), 131.5 (d, C*ortho* C_6H_5, $^2J_{CP}$ = 9.95 Hz), 153.3 (C*ortho* CNXylyl), 141.0 (d, H*C*=C, $^1J_{CP}$ = 28.73 Hz), 167.9 (d, C=*C*CO$_2$CH$_3$, $^2J_{CP}$ = 28.36 Hz), 170.3 (d, C=C*C*O$_2$CH$_3$, $^3J_{CP}$ = 23.57 Hz), 220.0 (*C*=N). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 84.1 (*P*Ph$_2$). Anal. Calcd for $C_{41}H_{49}NNbO_2PSi_2$: C, 64.13; H, 6.43; N, 1.82. Found: C, 64.00; H, 6.43; N, 1.85.

(4) Yield = 85%**.** IR (Nujol): ν (cm^{-1}) 1718 (COO), 1617 (C=N), 1588 (C=C). ^{1}H NMR (500 MHz, C_6D_6): δ 0.15 (s, 18 H, Si*Me*$_3$), 1.91 (s, 3 H, C*H*$_3$C=CCO$_2$CH$_3$), 2.33 (s, 6 H, C*H*$_3$, CNXylyl), 3.02 (s, 3H, C=CCO$_2$C*H*$_3$), 4.59, 4.70, 4.79, 5.33 (m, 2 H each complex signal, $C_5H_4SiMe_3$), 6.97 (m, 9H, *Ph*), 7.58 (t, 4 H, $^3J_{HH}$ = 7.68 Hz, P*Ph*$_2$), 7.62 (d, 1 H, $^2J_{HP}$ = 2.44 Hz, *H*C=C). ^{13}C{H} NMR (125 MHz, C_6D_6): δ 0.4 (Si*Me*$_3$), 20.0 (*C*H$_3$, CNXylyl), 30.0 (s, 3 H, *C*H$_3$C=CCO$_2$CH$_3$), 51.27 (C=CCO$_2$*C*H$_3$), 98.4 (C^1), 87.0, 95.6, 98.3, 106.5 (C$^{2\text{-}5}$, exact assignment not possible, $C_5H_4SiMe_3$), 121.5–128.4 (*C*$_6$H$_5$), 138.1 (d, C*ortho* *C*$_6$H$_5$, $^2J_{CP}$ = 33.84 Hz), 153.3 (C*ortho* CNXylyl), 141.1 (d, C*H*$_3$*C*=C, $^1J_{CP}$ = 29.41 Hz), 167.9 (d, C=*C*CO$_2$CH$_3$, $^2J_{CP}$ = 26.19 Hz), 170.3 (d, C=C*C*O$_2$CH$_3$, $^3J_{CP}$ = 23.77 Hz), 219.9 (*C*=N). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 101.1 (*P*Ph$_2$)). Anal. Calcd for $C_{42}H_{51}NNbO_2PSi_2$: C, 64.51; H, 6.57; N, 1.79. Found: C, 64.27; H, 6.24; N, 1.94 **.**