Table S1. Proton NMR spectroscopic data for triazenide-bridged complexes.[a]

Complex	^{1}H
[(η^4-cod)Rh(μ-RNNNR)$_2$Ir(CO)$_2$] **1**	7.54 (d, 4H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.42 (d, 4H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.14 (d, 4H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.03 (d, 4H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 4.19 (m, 4H, C$_8$*H$_{12}$*), 2.63 (m, br, 4H, C$_8$*H$_{12}$*), 2.35 (s, 6H, C*H$_3$*), 2.25 (s, 6H, C*H$_3$*), 2.10 (m, 2H, C$_8$*H$_{12}$*), 1.93 (m, 2H, C$_8$*H$_{12}$*)
[(OC)$_2$Rh(μ-RNNNR)$_2$Ir(CO)$_2$] **2**	7.52 (d, 4H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.49 (d, 4H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.09 (d, 8H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 2.30 (s, 12H, C*H$_3$*)
[(OC)(PPh$_3$)Rh(μ-RNNNR)$_2$Ir(CO)$_2$][b] **3**	7.63 (d, 2H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.58-7.46 {m, 8H, C$_6$*H$_4$* and P(C$_6$*H$_5$*)$_3$}, 7.43-7.28 {m, 9H, C$_6$*H$_4$* and P(C$_6$*H$_5$*)$_3$}, 7.25 (d, 2H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.11 (d, 4H, C$_6$*H$_4$*), 7.02 (d, 2H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 6.95 (d, 2H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 6.68 (d, 2H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 2.32 (s, 3H, C*H$_3$*), 2.27 (s, 6H, C*H$_3$*), 2.13 (s, 3H, C*H$_3$*)
[I(OC)$_2$Rh(μ-RNNNR)$_2$Ir(CO)$_2$I] **4**	7.18 (d, 4H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.15 (d, 4H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.11-7.03 (m, 8H, C$_6$*H$_4$*), 2.38 (s, 6H, C*H$_3$*), 2.35 (s, 6H, C*H$_3$*)
[NBu$^n_4$][I(OC)Rh(μ-RNNNR)$_2$Rh(CO)$_2$] [NBu$^n_4$]$^+$**5**$^-$	7.83 (d, 2H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.70-7.60 (m, 6H, C$_6$*H$_4$*), 6.95-6.90 (m, 6H, C$_6$*H$_4$*), 6.85 (d, 2H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 2.91 {t br, 8H, N(C*H$_2$*CH$_2$CH$_2$CH$_3$)$_4$}, 2.20 (s, 6H, C*H$_3$*), 2.18 (s, 3H, C*H$_3$*), 2.15 (s, 3H, C*H$_3$*), 1.42 {m br, 8H, N(CH$_2$C*H$_2$*CH$_2$CH$_3$)$_4$}, 1.27 {m br, 8H, N(CH$_2$CH$_2$C*H$_2$*CH$_3$)$_4$}, 0.88 {t, 12H, N(CH$_2$CH$_2$CH$_2$C*H$_3$*)$_4$}
[NBu$^n_4$][I$_2$(OC)Rh(μ-RNNNR)$_2$Rh(CO)I], [NBu$^n_4$]$^+$**6**$^-$	7.26 (d, 2H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.17 (d, 2H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.10-6.85 (m, 12H, C$_6$*H$_4$*), 2.97 {t br, 8H, N(C*H$_2$*CH$_2$CH$_2$CH$_3$)$_4$}, 2.26 (s, 6H, C*H$_3$*), 2.20 (s, 6H, C*H$_3$*), 1.50 {m br, 8H, N(CH$_2$C*H$_2$*CH$_2$CH$_3$)$_4$}, 1.36 {m br, 8H, N(CH$_2$CH$_2$C*H$_2$*CH$_3$)$_4$}, 0.94 {t, 12H, N(CH$_2$CH$_2$CH$_2$C*H$_3$*)$_4$}
[I(OC){RNNN(R)C(O)}Ir(μ-I)$_2$Ir{C(O)N(R)NNR}(CO)I] **7**	7.85 (d, 4H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.37 (d, 4H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.28 (d, 8H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 2.48 (s, 6H, C*H$_3$*), 2.37 (s, 6H, C*H$_3$*)
[Rh(RNNNR)I$_2$(CO)(PPh$_3$)] **8**	7.57-7.39 {m, 9H, P(C$_6$*H$_5$*)$_3$}, 7.32 (d, 2H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.28-7.18 {m, 6H, P(C$_6$*H$_5$*)$_3$}, 7.13 (d, 2H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 7.04 (d, 2H, $^1J_{HH}$ 9, C$_6$*H$_4$*), 6.73 (d, 2H, $^1J_{HH}$ 9,

	C_6H_4), 2.39 (s, 3H, CH_3), 2.33 (s, 3H, CH_3)

[a] Chemical shift (δ) in ppm, *J* values in Hz, spectra in CD_2Cl_2 at 20 °C. R = C_6H_4Me-*p*.