Interplay between an elusive 4-(isopropylamino)imidazol-2-ylidene and its isolable mesoionic tautomer, and associated reactivities

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**General Considerations**

All manipulations were performed under an inert atmosphere of dry nitrogen by using standard vacuum line and Schlenk tube techniques. Glassware was dried at 120°C in an oven for at least three hours. THF and diethyl ether were distilled from sodium/benzophenone, toluene from sodium. Pentane, dichloromethane and chloroform were dried over CaH₂ and subsequently distilled. NMR spectra were recorded on Bruker ARX250, AV300 or AV400 spectrometers. Chemical shifts are reported in ppm (δ) compared to TMS (1H and 13C) using the residual peak of deuterated solvent as internal standard.¹ Infrared spectra were obtained on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Microanalyses were performed by the Laboratoire de Chimie de Coordination Microanalytical Service and MS spectra by the mass spectrometry service of the Paul Sabatier University. N,N’-dimesitylformamidine,² [RhCl(1,5-COD)]₂,³ were synthesized according to literature procedures.

**Synthetic procedures**

**2-chloro-N-isopropylacetamide**

The reaction was carried out in an open flask without any special precaution. At 0°C, a solution of chloroacetyl chloride (4.0 mL, 50 mmol) in EtOAc (20 mL) was slowly added to a solution of isopropylamine (5.2 mL, 60 mmol, 1.2 eq.) and triethylamine (10.5 mmol, 75 mmol, 1.5 eq.) in EtOAc (50 mL). The ice-water bath was removed at the end of the addition and the reaction mixture was allowed to stir for 1 hour. The organic phase was washed with a solution of NH₄Cl (10% in water, 50 mL) and brine, dried over Na₂SO₄, filtered and evaporated using a rotary evaporator. The brown crude product was purified by a short bulb-to-bulb distillation (P ~ 0.1 mbar, T_bath up to 120°C)

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to give a white glassy solid (5.17 g, 76%). mp = 57°C; ¹H NMR (300 MHz, CDCl₃): δ = 6.36 (m, 1H, NH), 4.15-4.04 (m, 1H, CH(CH₃)₂), 4.02 (s, 2H, CH₂), 1.20 (d, 6H, J = 6.6 Hz, CH(CH₃)₂); ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ = 165.0 (CONH), 42.8 (CH₂), 42.1 (CH(CH₃)₂), 22.6 (CH(CH₃)₂); IR (ATR): ν = 3283 (NH), 3082, 2976, 2933, 1652 (CO), 1553 (NH), 1451, 1418, 1385, 1367, 1352, 1237, 1170, 1156, 1130, 937, 854, 771, 689 cm⁻¹; MS (ESI): m/z (%): 136 [M + H]⁺; 158 [M + Na]⁺; elemental analysis calc’d (%) for C₅H₁₀ClNO: C 44.29, H 7.43, N 10.33; found: C 44.18, H 7.60, N 10.12.

N-((isopropyl)-carbamoylmethyl)-N,N’-dimesitylformamidine (2)

N,N’-dimesitylformamidine (5.6 g, 20 mmol), 2-chloro-N-isopropylacetamide (3.25 g, 24 mmol, 1.2 eq.) and KI (330 mg, 2 mmol, 10 mol%) were placed in a Schlenk tube and DMF (40 mL) was added and then triethylamine (4.2 mL, 30 mmol, 1.5 eq.). The solution was stirred for 5 hours at 100°C and after cooling, was diluted with Et₂O (350 mL) and washed once with water (100 mL). The aqueous phase was extracted with additional Et₂O (100 mL) and the combined organic phases were washed again with water (2 x 50 mL) and brine (50 mL). After drying over Na₂SO₄, the crude solution was filtered and evaporated using a rotary evaporator. The beige crude product was purified by flash chromatography (SiO₂, hexane / EtOAc : 2 / 1, Rf = 0.64) to yield the pure product as a white powder (6.9 g, 91%). mp = 133°C; ¹H NMR (300 MHz, CDCl₃): δ = 7.98 (br, 1H, NH), 7.26 (s, 1H, N₂CH), 6.89 (s, 2H, CH₃Mes), 6.86 (s, 2H, CH₃Mes), 4.29 (s, 2H, CH₂), 4.15 (m, 1H, CH(CH₃)₂), 2.26 (s, 3H, CH₃ para), 2.25 (s, 3H, CH₃ para), 2.22 (s, 6H, CH₃ ortho), 2.20 (s, 6H, CH₃ ortho), 1.21 (d, 6H, J = 6.6 Hz, CH(CH₃)₂); ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ = 169.0 (C=O), 154.3 (N₂CH), 146.2, 139.6, 137.9 136.3, 131.9 (C_Mes), 129.1 (CH₃Mes), 129.0 (C_Mes), 128.6 (CH₃Mes), 54.7 (CH₂), 41.3 (CH(CH₃)₂), 22.7 (CH(CH₃)₂), 20.8, 20.7 (CH₃ p-Mes); 19.0, 18.1 (CH₃ o-Mes); IR (ATR): ν = 3252 (NH), 3076, 2969, 2917, 1637 (CO), 1606, 1560, 1479, 1319, 1260, 1227, 1206, 1144, 991, 851 cm⁻¹; MS (ESI): m/z
1,3-dimesityl-4-(isopropylamino)imidazolium triflate (3)

2,6-lutidine (1.57 mL, 13.5 mmol, 1.5 eq.) was added at room temperature to a solution of compound 2 (3.44 g, 9.0 mmol) in CH$_2$Cl$_2$ (65 mL) and the solution was cooled to -78°C. At this temperature, triflic anhydride (1.67 mL, 9.96 mmol, 1.1 eq.) was added dropwise and stirring was continued for 1.5 hours in the cooling bath. At this point, the latter was removed and the reaction mixture was allowed to warm to room temperature. A saturated solution of NaHCO$_3$ (50 mL) was added and the biphasic mixture was vigorously stirred for 5 min. The organic phase was separated and further washed with additional saturated NaHCO$_3$ (2 x 50 mL), dried over Na$_2$SO$_4$ and evaporated under vacuum. The pure imidazolium salt was precipitated from the light beige-yellow crude oil by adding Et$_2$O (150-200 mL) and ultrasonication. After drying, the product was isolated as a bright white powder (3.9 g, 84%). mp = 147°C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.69 (d, $J$ = 1.8 Hz, 1H, N$_2$CH), 7.09 (s, 2H, CH$_{Mes}$), 7.02 (s, 2H, CH$_{Mes}$), 6.43 (d, $J$ = 1.8 Hz, 1H, CH$_{Im-5}$), 3.54 (d, $J$ = 7.8 Hz, 1H, NH), 3.47-3.36 (m, 1H, CH(CH$_3$)$_2$), 2.37 (s, 3H, CH$_3$ para), 2.35 (s, 3H, CH$_3$ para), 2.18 (s, 6H, CH$_3$ ortho), 2.12 (s, 6H, CH$_3$ ortho), 1.20 (d, 6H, $J$ = 6.3 Hz, CH(CH$_3$)$_2$); $^{13}$C($^1$H) NMR (75.5 MHz, CDCl$_3$): $\delta$ = 142.2, 141.2, 140.6, 135.4, 134.2 (C$_{Mes}$), 131.1 (N$_2$CH), 130.5 (CH$_{Mes}$), 129.8 (CH$_{Mes}$), 126.1 (C$_{Im-4}$), 120.6 (q, $J_{CF}$ = 241 Hz, CF$_3$SO$_3$), 100.2 (CH$_{Im-5}$), 47.2 (CH(CH$_3$)$_2$), 22.1 (CH(CH$_3$)$_2$), 21.3, 21.2 (CH$_3$ para, 2H), 17.4, 17.2 (CH$_3$ para, 2H); IR (ATR): $\bar{v}$ = 3280 (NH), 3116, 3027, 2965, 2928, 1617, 1550, 1511, 1483, 1459, 1259, 1223, 1145, 1030, 853 cm$^{-1}$; MS (ESI): m/z (%):362 (100) [M - OTf]$^+$; elemental analysis calcd (%) for C$_{25}$H$_{32}$F$_3$N$_3$O$_3$S: C 58.69, H 6.30, N 8.21; found: C 58.74, H 6.70, N 8.14.

1,3-dimesityl-4-(isopropylamido)imidazolium (4 + 4’)

(%)380 (100) [M + H]$^+$, 332 (28), 310 (30), 281 (30) [Mes-NH-CH=NH-Mes]$^+$; elemental analysis calcd (%) for C$_{24}$H$_{33}$N$_3$O: C 75.59, H 8.76, N 11.07; found: C 76.40, H 8.88, N 10.86.
Imidazolium triflate 3 can be equally deprotonated with 1.05 equivalents of KOtBu at 0°C, KHMDS at 0°C or nBuLi at -78°C. For NMR characterization, procedure was as followed:

A solution of nBuLi in hexane (1.6 M, 48 µL, 81 µmol, 1.05 equiv.) was dropwise added to a solution of (IMes-NH$i$Pr)·HOTf (40 mg, 78 µmol) in THF (2 mL) at -78°C. The solution color changed from colorless to bright yellow. After 5 min., the cooling bath was removed and the reaction mixture was allowed to warm up to room temperature. After evaporation of volatiles, the yellow residue was dissolved in distilled THF-d8 (0.7 mL) and the solution was transferred to a screw-capped NMR tube (quantitative yield by NMR). $^1$H NMR (400 MHz, THF-d8): $\delta = 7.02$ (s, 4H, CH$_{Mes}$), 6.37 (br s, 1H, CH$_{Im-5}$), 3.26 (sept, $J = 6.7$ Hz, 1H, CH(CH$_3$)$_2$), 2.30 (s, 6H, CH$_3$ para), 2.14 (s, 6H, CH$_3$ ortho), 2.08 (s, 6H, CH$_3$ ortho), 1.07 (d, $J = 6.7$ Hz, 6H, CH(CH$_3$)$_2$); $^{13}$C {$^1$H} NMR (100.5 MHz, THF-d8): $\delta = 145.2$ (br, N$_2$CH), 140.5, 140.4, 136.6, 135.3, 134.0, 130.3 (C$_{Mes}$ + C$_{Im-4}$), 130.0 (CH$_{Mes}$), 129.8 (CH$_{Mes}$), 121.7 (q, $J_{CF} = 321$ Hz, CF$_3$SO$_3$ by-product), 97.7 (br, CH$_{Im-4}$), 48.5 (CH(CH$_3$)$_2$), 22.6 (CH(CH$_3$)$_2$), 21.1, 20.9 (CH$_3$ p-Mes); 17.8, 17.0 (CH$_3$ o-Mes).

**Lithium 1,3-dimesityl-4-(isopropylamido)imidazol-2-ylidene**

A solution of nBuLi in hexane (1.6 M, 98 µL, 0.156 mmol, 2.0 equiv.) was dropwise added to a solution of (IMes-NH$i$Pr)·HOTf (40 mg, 78 µmol) in THF (3 mL) at -78°C. The colorless solution turned bright yellow. At the end of addition, the cooling bath was removed and the reaction mixture was allowed to warm up to room temperature, and turned to a clear dark red solution. After evaporation of volatiles, the red residue was dissolved in distilled THF-d8 (0.7 mL) and the solution was transferred to a screw-capped NMR tube. $^1$H NMR (300 MHz, THF-d8): $\delta = 6.95$ (s, 2H, CH$_{Mes}$), 6.85 (s, 2H, CH$_{Mes}$), 5.12 (s, 1H, CH$_{Im-5}$), 2.92 (sept, $J = 6.7$ Hz, 1H, CH(CH$_3$)$_2$), 2.27 (s, 3H, CH$_3$ para), 2.24 (s, 3H, CH$_3$ para), 2.15 (s, 6H, CH$_3$ ortho), 2.08 (s, 6H, CH$_3$ ortho), 0.94 (d, $J = 6.7$ Hz, 6H, CH(CH$_3$)$_2$); $^{13}$C {$^1$H} NMR (75.5 MHz, THF-d8): $\delta = 155.1$ (C$_{Im-4}$), 140.8, 137.7, 136.9, 136.7, 136.5 (C$_{Mes}$), 129.8 (CH$_{Mes}$), 128.8 (CH$_{Mes}$), 121.5 (q, $J_{CF} = 320$ Hz, CF$_3$SO$_3$), 89.4 (CH$_{Im-4}$), 50.9 (CH(CH$_3$)$_2$), 24.0 (CH(CH$_3$)$_2$), 20.9, 20.8 (CH$_3$ p-Mes); 18.7, 17.6 (CH$_3$ o-Mes).
The signal corresponding to the carbenic carbon atom could not be located in the $^{13}$C NMR spectrum, likely due to coupling and quadrupolar relaxation caused by the lithium nuclei. Such a behavior was already observed with an anionic six-membered NHC by Roesler and co-workers.$^4$ The chemical shift of $C_{Im-4}$ at $\delta = 155.1$ ppm is comparable to the one of the $C_{Im-4}$ ($\delta = 154.4$ ppm) of the corresponding anionic imidazol-2-ylidene-4-olate reported by Glorius and co-workers.$^5$

### 1,3-dimesityl-4-(isopropylamino)imidazolin-2-thione (5)

Compound 3 (141 mg, 0.276 mmol) was dissolved in THF (5 mL) and KOTBu (34 mg, 0.304 mmol, 1.1 eq.) was added all at once as a solid at room temperature. The solution color became first yellow and then turned to dark orange. After 15 min. at room temperature, sulfur (13 mg, 0.414 mmol, 1.5 eq.) was added, and after additional 30 min. of stirring, all volatiles were evacuated in vacuo. The residue was purified by a rapid flash chromatography (SiO$_2$, hexane/EtOAc : 4/1) to give the thiourea as a pale yellow foam (75 mg, 69%). Mp = 80°C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.03$ (s, 2H, CH$_{Mes}$), 6.97 (s, 2H, CH$_{Mes}$), 5.85 (s, 1H, CH$_{Im-5}$), 3.33-3.21 (m, 1H, CH(CH$_3$)$_2$), 2.58 (d, $J = 7.8$ Hz, 1H, NH), 2.34 (s, 3H, CH$_3$ para), 2.31 (s, 3H, CH$_3$ para), 2.18 (s, 6H, CH$_3$ ortho), 2.15 (s, 6H, CH$_3$ ortho), 1.13 (d, 6H, $J = 6.6$ Hz, CH(CH$_3$)$_2$); $^{13}$C{$_1$H} NMR (75.5 MHz, CDCl$_3$): $\delta = 158.2$ (N$_2$C=S), 139.9, 139.0, 137.1, 136.5, 136.0 (C$_{Mes}$), 129.9 (CH$_{Mes}$), 129.4 (CH$_{Mes}$), 95.0 (CH$_{Im-5}$), 46.5 (CH(CH$_3$)$_2$), 22.7 (CH(CH$_3$)$_2$), 21.5, 21.4 (CH$_3$ p-Mes); 18.2, 17.9 (CH$_3$ o-Mes); IR (ATR): $\tilde{\nu} = 2968, 2920, 2861, 1746, 1663, 1630, 1610, 1485, 1436, 1384, 1322, 1302, 1281, 1195, 1174, 1146, 1034, 1013, 849, 837, 801, 669$ cm$^{-1}$; MS (ESI): m/z (%): 394 (17) [M + H]$^+$, 362 (100) [M + H – S]$^+$; HR-MS (ESI): m/z: calcd for C$_{24}$H$_{32}$N$_3$S: 394.2317; found: 394.2321.

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(IMes-NHiPr)-CS₂ (6)

Compound 3 (123 mg, 0.25 mmol) was added as a solid all at once to a solution of potassium tert-butoxide (29.5 mg, 0.263 mmol, 1.05 equiv.) in THF (5 mL) at 0°C. After 10 min., carbon disulfide (30 µL, 2.0 equiv.) was added to the yellow solution which became dark red at the end of the addition. After 1 hour at room temperature, volatiles were removed in vacuo and the crude product was purified by flash chromatography (SiO₂, CH₂Cl₂/MeOH : 98/2) to yield a dark red powder (39 mg, 36%). Mp = 114°C; ¹H NMR (400 MHz, CDCl₃): δ = 6.96 (s, 2H, CHMes), 6.89 (s, 2H, CHMes), 5.98 (s, 1H, CHIm₅), 3.42-3.34 (m, 1H, CH(CH₃)₂), 2.93 (d, J = 7.6 Hz, 1H, NH), 2.34 (s, 6H, CH₃ortho), 2.32 (s, 6H, CH₃ortho), 2.29 (s, 3H, CH₃para), 2.27 (s, 3H, CH₃para), 1.19 (d, 6H, J = 6 Hz, CH(CH₃)₂); ¹³C{¹H} NMR (100.5 MHz, CDCl₃): δ = 222.8 (CS₂), 143.7, 141.1, 140.0, 137.0, 136.9, 135.8, 131.6 (Cq), 130.0 (CHMes), 129.3 (CHMes), 126.7 (Cq), 95.2 (CHIm₅), 46.8 (CH(CH₃)₂), 22.4 (CH(CH₃)₂), 21.2, 21.1 (CH₃p-Mes); 18.7, 18.5 (CH₃o-Mes); IR (ATR): ν = 2967, 2917, 1857, 1622, 1496, 1462, 1440, 1418, 1377, 1217, 1167, 1138, 1056, 1042, 1016, 880, 849, 723 cm⁻¹; MS (ESI): m/z (%): 438 (100) [M + H]⁺; HR-MS (ESI): m/z: calcd for C₂₅H₃₂N₃S₂: 438.2038; found: 438.2043.

Chloro(η⁴-1,5-cyclooctadiene)(1,3-dimesityl-4-(isopropylamino)imidazol-2-ylidene)Rhodium(I) (7)

[RhCl(COD)]₂ (79.5 mg, 0.161 mmol, 0.5 eq.) and KOT/Bu (40 mg, 0.354 mmol, 1.1 eq.) were reacting in THF (6 mL) for 15 min. at room temperature. Then, imidazolium triflate 3 (165 mg, 0.322 mmol) was added as a solid. After 1 hour, full conversion was confirmed by a ¹H NMR experiment on a small sample. All volatiles were thus evaporated under vacuum and the residue was purified by a rapid filtration through a pad of neutral Al₂O₃ Brockmann type III (length ~ 7 cm) under N₂, to yield after evaporation
and drying a bright yellow foam (183 mg, 93%). Single crystals suitable for an X-Ray diffraction experiment were grown from slow diffusion of pentane into a saturated solution of 7 in EtOAc at low temperature (-80°C). Mp = 178°C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.08-7.01\) (br, 3H, \(CH_{Mes}\)), 6.96 (s, 1H, \(CH_{Mes}\)), 6.05 (s, 1H, \(CH_{Im-5}\)), 4.45 (br, 2H, \(CH_{COD}\)), 3.33 (br, 1H, \(CH_{COD}\)), 3.25 (br, 1H, \(CH_{COD}\)), 3.16 (m, 1H, \(CH(CH_3)_2\)), 2.57 (d, \(J = 7.5\) Hz, 1H, \(NH\)), 2.46 (s, 3H, \(CH_3\)), 2.39 (s, 3H, \(CH_3\)), 2.36 (s, 6H, \(CH_3\)), 2.12 (s, 6H, \(CH_3\)), 1.83-1.78 (m, 4H, \(CH_2\)), 1.60-1.42 (m, 4H, \(CH_2\)), 1.08 (d, 6H, \(J = 6.3\) Hz, \(CH(CH_3)_2\)); \(^{13}\)C{\(^1\)H} NMR (100.5 MHz, CDCl\(_3\)): \(\delta = 176.8\) (d, \(J_{RhC} = 53\) Hz, \(N_2C\)), 140.7, 139.2, 139.0, 138.3, 137.8, 137.0, 135.9, 134.6, 132.0 (C\(_q\)), 130.1 (C\(_{HMes}\)), 129.7 (C\(_{Mes}\)), 128.6 (C\(_{Mes}\)), 128.1 (C\(_{Mes}\)), 101.5 (C\(_{Im-5}\)), 95.9 (br, \(CH_{COD}\)), 95.3 (br, \(CH_{COD}\)), 68.1 (d, \(J_{RhC} = 18\) Hz, \(CH_{COD}\)), 66.9 (d, \(J_{RhC} = 21\) Hz, \(CH_{COD}\)), 47.0 (CH(CH\(_3\)_2)), 33.3 (CH\(_2\)COD)), 32.4 (CH\(_2\)COD)), 28.9 (CH\(_2\)COD)), 28.2 (CH\(_2\)COD)), 22.6 (CH(CH\(_3\)_2)), 21.4, 21.2, 19.9, 18.3, 18.2 (CH\(_3\))); IR (ATR): \(\tilde{\nu} = 3265, 2963, 2915, 2872, 2826, 1633, 1609, 1481, 1382, 1368, 1314, 1302, 1218, 1171, 1144, 1127, 1033, 992, 953, 917, 849, 727, 708 \text{ cm}^{-1}\); MS (ESI): m/z (%): 572 (100) [M − Cl]; elemental analysis \(\text{calcd (\%)}\) for C\(_{32}\)H\(_{43}\)ClN\(_3\)Rh: C 62.20, H 7.03, N 6.77; \(\text{found: C} 62.28, \text{H} 7.20, \text{N} 6.55.\)

Chloro(\(\eta^4\)-1,5-cyclooctadiene)(1,3-dimesityl-4-(isopropylimino)-5-oxo-imidazolin-2-ylidene)Rhodium(I) (8)

Under air, RhCl(COD)(4) (34 mg, 55.9 \(\mu\)mol) was dissolved in non-distilled CH\(_2\)Cl\(_2\) and Si\(_2\)O\(_2\) was added into the round-bottom flask and the mixture was stirred 5 min before removal of volatiles. The solution turned from bright yellow to dark red during this time. The adsorbed product was loaded onto a silica gel column and was purified using CH\(_2\)Cl\(_2\)/hexane (10/1) as eluting system. The oxidized complex was isolated as a dark red powder (30 mg, 87%). Single crystals suitable for an X-Ray diffraction experiment were grown from slow diffusion of pentane into a saturated solution of 8 in CH\(_2\)Cl\(_2\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.09\) (s, 2H, \(CH_{Mes}\)), 7.03 (s, 1H, \(CH_{Mes}\)), 6.99 (s, 1H, \(CH_{Mes}\)), 5.17 (sept, \(^3J = 6.4\) Hz, 1H, \(CH(CH_3)_2\)), 4.89-4.84 (m, 1H, \(CH_{COD}\)), 4.82-4.76 (m, 1H, \(CH_{COD}\)), 3.54-3.50 (m, 1H, \(CH_{COD}\)), 3.47-3.41
Chlorodicarbonyl(1,3-dimesityl-4-(isopropylamino)imidazol-2-ylidene)rhodium(I) (10)

CO gas was bubbled into a solution of 7 (63.5 mg, 0.104 mmol) in CH2Cl2 (5 mL) for 10 min during which the color changed from bright yellow to very pale yellow. After 30 minutes, all volatiles were removed under vacuum and the residue was washed with pentane (5 mL) to yield after drying a pale beige powder (48 mg, 83%).

Mp = 175-178°C; 1H NMR (400 MHz, CDCl3): δ = 7.03 (s, 2H, CHMes), 6.98 (s, 2H, CHMes), 6.19 (s, 1H, CHIm-5), 3.29-3.20 (m, 1H, CH(CH3)2), 2.70 (d, J = 7.6 Hz, 1H, NH), 2.37 (s, 3H, CH3Mes), 2.35 (s, 3H, CH3Mes), 2.27 (s, 6H, CH3Mes), 2.21 (s, 6H, CH3Mes), 1.12 (d, 6H, J = 6.4 Hz, CH(CH3)2); 13C {1H} NMR (100.5 MHz, CDCl3): δ = 185.3 (d, 1JRhC = 53.6 Hz, CO), 183.1 (d, 1JRhC = 74.9 Hz, CO), 170.2 (d, 1JRhC = 44.8 Hz, N2C), 140.9, 139.9, 139.0, 136.6, 135.9, 135.5, 130.8 (Cq), 129.8 (CHMes), 129.2 (CHMes), 101.2 (CHIm-5), 47.0 (CH(CH3)2), 22.5 (CH(CH3)2), 21.4, 21.3 (CH3p-Mes), 18.6, 18.5 (CH3 o-Mes); IR (ATR): ν = 2972, 2920, 2861, 1980, 1633, 1609, 1483, 1385, 1372, 1324, 1173, 1146, 1032, 854, 708 cm⁻¹; MS (ESI): m/z (%): 533 (100) [Rh(CO)(CH3CN)(IMes-NHPr)]⁺; HR-MS (ESI): m/z: calcd for C27H34N4ORh: 533.1788; found: 533.1794.

Electronic Supplementary Material (ESI) for Chemical Communications
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Chlorodicarbonyl(1,3-dimesityl-4-(isopropylimino)-5-oxoimidazolin-2-ylidene)rhodium(I) \((11)\) and Chlorocarbonyl(1,3-dimesityl-4-(isopropylimino)-5-oxoimidazolin-2-ylidene)rhodium(I) dimer \((12)\)

CO gas was bubbled into a solution of \(8\) (51 mg, 0.082 mmol) in \(\text{CH}_2\text{Cl}_2\) (5 mL) for 10 min during which the color changed from dark red to pale yellow. After 30 minutes, all volatiles were removed under vacuum. The color of the mixture was seen to darken during this operation. A small sample of the dicarbonyl complex could be isolated by washings with pentane (2 x 5 mL, dark red solution) and rapid drying of the pale yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.03\) (s, 2H, \(\text{C}_\text{H}_{\text{Mes}}\)), 7.01 (s, 2H, \(\text{C}_\text{H}_{\text{Mes}}\)), 5.24-5.21 (m, 1H, \(\text{C}_\text{H}(\text{CH}_3)_{2}\)), 2.38 (s, 3H, \(\text{C}_\text{H}_3\text{p-Mes}\)), 2.36 (s, 3H, \(\text{C}_\text{H}_3\text{p-Mes}\)), 2.30 (s, 6H, \(\text{C}_\text{H}_3\text{o-Mes}\)), 2.26 (s, 6H, \(\text{C}_\text{H}_3\text{o-Mes}\)), 1.19 (d, 6H, \(J = 6\) Hz, \(\text{CH}(\text{CH}_3)_{2}\)); \(^{13}\)C\{\(^1\)H\} NMR (100.5 MHz, CDCl\(_3\)): \(\delta = 224.4\) (d, \(^1\)\(J_{\text{RhC}} = 44.8\) Hz, N\(_2\)C), 184.3 (d, \(^1\)\(J_{\text{RhC}} = 52.8\) Hz, Rh-CO), 182.1 (d, \(^1\)\(J_{\text{RhC}} = 73.9\) Hz, Rh-CO), 151.8 (C=O), 140.4, 140.1, 138.8, 136.0, 132.0, 130.1 (C\(_q\)), 129.8 (CH\(_{\text{Mes}}\)), 129.7 (CH\(_{\text{Mes}}\)), 128.8 (C\(_q\)), 50.6 (CH(CH\(_3\))\(_2\)), 23.9 (CH(CH\(_3\))\(_2\)), 21.5, 21.4, 19.0, 18.7 (CH\(_{\text{Mes}}\)); IR (\(\text{CH}_2\text{Cl}_2\)): \(\tilde{\nu} = 2092\) (CO\(_{\text{syn}}\)), 2009 (CO\(_{\text{anti}}\)) cm\(^{-1}\).

For isolation of the mono-carbonylated dimer \(12\), the dark red washing solution and the yellow solid were collected together and dissolved in \(\text{CH}_2\text{Cl}_2\) and the solution was evaporated under vacuum. This operation was carried out a second time to secure a complete conversion of the di-carbonyl complex [RhCl(CO)(\(9\))] into the dimer [RhCl(CO)(\(9\))]\(_2\). A dark red powder was obtained after solubilisation in pentane (4 mL) and precipitation at \(-80^\circ\text{C}\) (33 mg, 75%).\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 6.94\) (br, 4H, \(\text{C}_\text{H}_{\text{Mes}}\)), 5.14-5.08 (m, 1H, \(\text{CH}(\text{CH}_3)_{2}\)), 2.35 (s, 3H, \(\text{CH}_3\text{p-Mes}\)), 2.33 (s, 3H, \(\text{CH}_3\text{p-Mes}\)), 2.19 (s, 6H, \(\text{CH}_3\text{o-Mes}\)), 2.14 (s, 6H, \(\text{CH}_3\text{o-Mes}\)), 1.11 (d, 6H, \(J = 6\) Hz, \(\text{CH}(\text{CH}_3)_{2}\)); \(^{13}\)C\{\(^1\)H\} NMR (100.5 MHz, CDCl\(_3\)): \(\delta = 218.7\) (d, \(^1\)\(J_{\text{RhC}} = 60.1\) Hz, N\(_2\)C), 183.0 (d, \(^1\)\(J_{\text{RhC}} = 54.5\) Hz, Rh-CO), 152.1 (C=O), 139.4, 139.0, 136.1, 136.0, 132.9, 130.9 (C\(_q\)), 129.6 (CH\(_{\text{Mes}}\)), 129.4 (CH\(_{\text{Mes}}\)), 49.8 (CH(CH\(_3\))\(_2\)), 23.8 (CH(CH\(_3\))\(_2\)), 21.4, 21.3 (CH\(_3\)o-Mes), 19.2,
19.1 (CH$_3$Mes); IR (C): $\tilde{\nu} = 2092, 2009$ cm$^{-1}$; IR (ATR mode): $\tilde{\nu} = 2970, 2920, 2851, 1987, 1745, 1668, 1609, 1484, 1367, 1305, 1271, 1192, 1167, 1145, 1093, 1032, 851, 829, 793$ cm$^{-1}$; MS (ESI, CH$_3$CN): m/z (%): 547 (100) [Rh(CO)(CH$_3$CN)(SIMes(NiPr)(=O))]$^+$; HR-MS (ESI): m/z: calcd for C$_{27}$H$_{32}$N$_4$O$_2$Rh: 547.1580; found: 547.1577.

X-ray Diffraction Studies

Crystals of 3, 4', 7, and 8 suitable for X-ray diffraction were obtained through recrystallization from dichloromethane/ether (3), benzene/pentane (4'), diethyl acetate/pentane (7), or dichloromethane/pentane. Data were collected on a Bruker D8 Apex 2 diffractometer. All calculations were performed on a PC-compatible computer using the WinGX system. The structures were solved by using the SIR92 program, which revealed in each instance the position of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses by using the SHELXL97 program. Atomic scattering factors were taken from the usual tabulations. Anomalous dispersion terms for Rh, Cl, or S atoms were included in $F_c$. All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms – except NH in the structures of 3, 7, and 8 and HC=CH atoms of the COD ligand in 7 and 8 – were set in idealized position (R$_3$CH, C-H = 0.96 Å; R$_2$CH$_2$, C-H = 0.97 Å; RCH$_3$, C-H = 0.98 Å; C(sp$^3$)-H = 0.93 Å; U$_{iso}$ 1.2 or 1.5 time greater than the U$_{eq}$ of the carbon atom to which the hydrogen atom is attached) and their position were refined as “riding” atoms. NH and HC=CH hydrogen atoms in the structures of 3, 7, or 8 were located from difference Fourier maps; their position were refined but not

their U_{iso}, which were fixed to 1.2 time the U_{eq} of the carbon atom to which the hydrogens atoms were attached.

Complex 7 was found to crystallize as two independent molecules (molecule A and molecule B) per unit cell. In the final stages of the refinement, Fourier maps showed an isolated peak in the vicinity of N3b and Cl1a, which finally refined in a satisfactory manner as an oxygen atom with a s.o.f. of 0.5; it has been attributed to a water molecule statistically located between these to atoms. However, the corresponding hydrogen atoms could not be located in an unambiguous manner and were not included in the final refinement.

The crystal of 8 used for data collection was found to display non-merohedral twinning. Both components of the twin were indexed with the program CELL_NOW. The second twin component can be related to the first component by 180 deg rotation around the a axis. Integrated intensities for the reflections from the two components were written into a SHELXL-93 HKLF 5 reflection file with the data integration program TWINABS using all reflection data (exactly overlapped, partially overlapped and non-overlapped).

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10 Twinabs (V1.05); Bruker AXS Inc., Madison, WI, 2004.
Molecular structure of imidazolium triflate 3
$^1$H NMR spectrum of ClCH$_2$C(=O)NH$i$Pr (300MHz, CDCl$_3$)

$^{13}$C{$^1$H} NMR spectrum of ClCH$_2$C(=O)NH$i$Pr (75MHz, CDCl$_3$)
$^1$H NMR spectrum of (IMes-NH$i$Pr)-HOTf (3) (300MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum of (IMes-NH$i$Pr)-HOTf (3) (75MHz, CDCl$_3$)
$^1$H NMR spectrum of (IMes-NiPr)·H (4') (400 MHz, THF-d8, 298 K)

$^{13}$C($^1$H) NMR spectrum of (IMes-NiPr)·H (4') (100.5 MHz, THF-d8, 298 K)
$^1$H NMR spectrum of (IMes-N\textsubscript{i}Pr)-Li (300 MHz, THF-d8)

$^{13}$C\textsubscript{($^1$H)} NMR spectrum of (IMes-N\textsubscript{i}Pr)-Li (75.5 MHz, THF-d8)
$^1$H NMR spectrum of (IMes-NH$_2$Pr)=S (5) (300 MHz, CDCl$_3$)

$^{13}$C$^1$H NMR spectrum of (IMes-NH$_2$Pr)=S (5) (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of (IMes-NH$iPr$)-CS$_2$ (6) (400 MHz, CDCl$_3$)

$^{13}$C{$^1$H} NMR spectrum of (IMes-NH$iPr$)-CS$_2$ (6) (100.5 MHz, CDCl$_3$)
$^1$H NMR spectrum of RhCl(COD)(IMes-NH$^i$Pr) (7) (300 MHz, CDCl$_3$)

$^{13}$C{$^1$H} NMR spectrum of RhCl(COD)(IMes-NH$^i$Pr) (7) (75.5 MHz, CDCl$_3$)
$^1$H NMR spectrum of RhCl(COD)(SIMes(=O)(=N\text{i}Pr)) (8) (400 MHz, CDCl$_3$)

$^{13}$C{$^1$H} NMR spectrum of RhCl(COD)(SIMes(=O)(=N\text{i}Pr)) (8) (100.5 MHz, CDCl$_3$)
$^1$H NMR spectrum of RhCl(CO)$_2$(IMes-NH$i$Pr) (10) (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum of RhCl(CO)$_2$(IMes-NH$i$Pr) (75.5 MHz, CDCl$_3$)
$^1$H NMR spectrum of [RhCl(CO)(SIMes(=O)(=NiPr))]$_2$ (12) (400 MHz, CDCl$_3$)

$^{13}$C{$^1$H} NMR spectrum of [RhCl(CO)(SIMes(=O)(=NiPr))]$_2$ (12) (100.5 MHz, CDCl$_3$)