Supporting information for the paper entitled:

A Closed-Shell Monomeric Rhenium(1-) Anion Provided by *m*-Terphenyl Isocyanide Ligation

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Synthetic Procedures.

General considerations. All manipulations were carried out under an argon atmosphere using standard Schlenk and glovebox techniques. Unless otherwise stated, reagent-grade starting materials were purchased from commercial sources and either used as received or purified by standard procedures. Solvents were dried and deoxygenated according to standard procedures. Benzene-d_6 was distilled from NaK alloy and stored under Ar prior to use. Celite 405 (Fisher Scientific) was dried at a temperature above 250℃ and stored in the glovebox prior to use. The ligand $CNAr^{Dipp2}$ was prepared as previously described.[1]

NMR spectra were recorded at 20°C with a JEOL 400 MHz multinuclear spectrometer. Positive- and negative-mode ESI mass spectra were measured with an Agilent 6210 ESI-TOF (Agilent Technology) mass spectrometer. The EPR spectrum of $[Re(CO)_3(CNAr^{Dipp2})_2]$ was recorded in the X-band at 78 K in THF with a Magnetech Miniscope spectrometer. Simulations were done with *Easyspin*.[2] Elemental analysis of carbon, hydrogen, nitrogen and sulfur were performed using a Heraeus elemental analyzer. For the IR spectra a Nicolet iS10 FT-IR spectrometer was used. The following abbreviations were used for the intensities and characteristics of IR absorption bands: vs = very strong, s = strong, w = weak.

Synthesis of *cis,fac*-$[Re(CO)_3Br(CNAr^{Dipp2})_2]$. $CNAr^{Dipp2}$ (60 mg, 0.142 mmol, 2.5 equiv) was added to a solution of $[Re(CO)_5Br]$ (23 mg, 0.057 mmol) in 6 mL THF. The resulting solution was heated under reflux under an Ar atmosphere for 24 h. The resulting mixture was concentrated and MeOH was added. Storage at 4 °C for 12 h resulted in the formation of pale yellow crystals of *cis,fac*-$[Re(CO)_3Br(CNAr^{Dipp2})_2]$, which were collected and dried *in vacuo*. The formation of significant amounts of the *trans,mer*-$[Re(CO)_3Br(CNAr^{Dipp2})_2]$ isomer was not observed under such conditions. Crystals suitable for X-Ray structure determination were grown from a CH_2Cl_2/hexane solution at -35°C. Yield: 133 mg, (60%). ^{1}H NMR (CD_2Cl_2, ppm): δ = 7.48 (t, 2H, *J* = 8 Hz, *p*-Ar), 7.35 (t, 4H, *J* = 8 Hz, *p*-Dipp), 7.23 (d, 4H, *J* = 8 Hz, *m*-Ar), 7.20-7.15 (two m, 8H, *m*-Dipp), 2.46 (sept, 8H, *J* = 7 Hz, C*H*$(CH_3)_2$), 1.08 (d, 12H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.05 (d, 12H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.03 (d, 24H, *J* = 7 Hz, CH(C*H*$_3)_2$). ^{13}C{1H} NMR (THF, ppm) δ = 186.1 (*C*≡O), 182.4 (*C*≡N), 146.68, 146.52, 140.80, 135.12, 131.90, 130.14, 129.84, 128.12, 124.41, 124.36, 31.98-31.97 (CH-*C*H$_3$), 25.14 (*C*H-CH$_3$), 24.86 (*C*H-CH$_3$), 24.84 (*C*H-CH$_3$), 24.72 (*C*H-CH$_3$). FTIR (KBr) ν_{max} = 2164w and 2119vs (CN), 2024vs, 1977vs and 1931vs (CO), also 2960s, 2867w, 1580w, 1459s, 1412w, 1384w, 1362w, 1328w, 1252w, 1179w, 1105w, 1056w, 935w, 822w, 802w, 822s, 792s, 753vs, 689w, 613w, 585w, 548w cm^{-1}. Elemental analyses: Found: C, 65.5; H 6.3; N, 2.3. Calc. for $C_{65}H_{74}BrN_2O_3Re$: C 65.2; H 6.2; N 2.3%. MS ESI+: *m*/*z* 1219.4338 (calc. for M + Na$^+$, 1219.4338), 1235.4073 (calc. for M + K$^+$, 1235.4077), also: 1117.5263 (calc. for M – Br$^-$, 1117.5257), 1254.5111 (calc. for M + Me_3CH + H$^+$, 1254.5223).

Synthesis of *trans,mer*-$[Re(CO)_3Br(CNAr^{Dipp2})_2]$. $CNAr^{Dipp2}$ (160 mg, 0.378 mmol) was added to a solution of $[Re(CO)_5Br]$ (77 mg, 0.189 mmol) in 10 mL toluene. The resulting solution was heated under reflux for 12 h. The resulting mixture was concentrated and chloroform was added. Storage at 4 °C resulted in pale yellow crystals of *trans,mer*-$[Re(CO)_3Br(CNAr^{Dipp2})_2]$, which were collected and dried *in vacuo*. Yield: 60 mg (88%). Crystals suitable for X-Ray structure determination were obtained from a $CHCl_3$/toluene solution. ^{1}H NMR (CD_2Cl_2, ppm): δ = 7.49 (t, 2H, *J* = 8 Hz, *p*-Ar), 7.35 (t, 4H, *J* = 8 Hz, *p*-Dipp), 7.27 (d, 4H, *J* = 8 Hz, *m*-Ar), 7.20 (d, 8H, *J* = 8 Hz, *m*-Dipp), 2.45 (sept, 8H, *J* = 7 Hz, C*H*$(CH_3)_2$), 1.09 (d, 24H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.08 (d, 24H, *J* = 7 Hz, CH(C*H*$_3)_2$). FTIR (KBr) ν_{max} = 2121vs (CN), 1986vs and 1922vs (CO), also 2959s, 2925w, 2866w, 2064w, 1580w, 1461s, 1413w, 1381w, 1361w, 1328w, 1251w, 1177w, 1105w, 1054w, 936w, 824w, 801s, 753s, 689w, 626w, 604s,

583s. Elemental analyses: Found: C, 65.5; H 6.3; N, 2.3. Calc. for $C_{65}H_{74}BrN_2O_3Re$: C 64.7; H 6.2; N 2.1 %. MS ESI+: *m*/*z* 1219.4338 (calc. for M + Na^+, 1219.4338), 1235.4073 (calc. for M + K^+, 1235.4077).

Synthesis of K[Re(CO)$_3$(CNAr^{Dipp2})$_2$]. A freshly prepared suspension of KC_8 in THF (0.2 mmol, 6 mL) was added in two portions over 1 h with intermittent stirring to a thawing solution of *cis*,*fac*-[Re(CO)$_3$Br(CNAr^{Dipp2})$_2$] (60 mg, 0.05 mmol) in 4 mL THF. During this time, the solutions were periodically refrozen by placement into a glovebox cold well. After the addition was complete, the reaction mixture was allowed to warm to room temperature. All volatile materials were removed *in vacuo*. The resulting residue was then dispersed in toluene and filtered over celite. The filtrate was concentrated and layered with pentane. Storage at -35 °C resulted in the formation of dark red single crystals, which were suitable for X-Ray structure determination. Estimated yield: 50%. ^{1}H NMR (CD_2Cl_2, ppm): δ = 7.31 (t, 4H, *J* = 8 Hz, *p*-Dipp), 7.18-7.12 (d, 8H, *J* = 8 Hz, *m*-Dipp, overlapping with the C_6H_6 signal), 6.97 (d, 4H, *J* = 8 Hz, *m*-Ar), 6.92-6.86 (t, 2H, *J* = 8 Hz, *p*-Ar), 2.79 (sept, 8H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 1.27 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.07 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$). FTIR (KBr) ν_{max} = 1912vs (CN, broad), 1800 and 1749 (CO, broad), also 3058w, 2959s, 2927s, 2866s, 2236w, 2114w, 1574s, 1500w, 1460s, 1411s, 1383w, 1361w, 1328w, 1251w, 1178w, 1104w, 1055s, 934w, 823w, 805w, 789w, 755s, 688w, 600w, 585w, 554w, 516w, 477w, 436w, 419w.

Synthesis of [Re(CO)$_3$(CNAr^{Dipp2})$_2$].

cis,*fac*-[Re(CO)$_3$Br(CNAr^{Dipp2})$_2$] (60 mg, 0.05 mmol) was dissolved in THF (4 mL) and 0.1% Na/Hg (Na: 0.1 g; Hg: 9.9 g; 87 equiv Na/Re) was added. The mixture was vigorously stirred for 24 h. The solution was decanted and the solvent removed under reduced pressure. The solid residue was dispersed in Et_2O/Pentane and filtered over celite. All volatile material were removed and the solid was dried *in vacuo*. FTIR (KBr) ν_{max} = 2083vs (CN), 1966vs, 1948vs and 1913s (CO), also 2960vs, 2927w, 2867w, 2004w, 1845w, 1749w, 1577w, 1460w, 1415w, 1383w, 1362w, 1329w, 1252w, 1178w, 1055w, 936w, 803w, 790w, 755w, 689w, 602w, 584w, 565w, 525w, 469w, 440w. EPR (THF, 78 K): (g_x = 2.1386, g_y = 2.0585, g_z = 2.0203, $A^{Tc}_x = 32 \cdot 10^{-4}$ cm^{-1}, $A^{Tc}_y = 20 \cdot 10^{-4}$ cm^{-1}, $A^{Tc}_z = 404 \cdot 10^{-4}$ cm^{-1}).

Crystallographic Structure Determinations

General. The intensities for the X–ray determinations were collected on a Bruker D8 Venture or on a Bruker APEX II Ultra instrument with Mo Kα radiation. Structure solution and refinement were performed with the SHELX program packages.[3,4] Hydrogen atoms were placed at calculated positions and treated with the 'riding model' option of SHELXL. The representation of molecular structures was done using the program DIAMOND (vers. 4.5.1).[5] Additional information on the structure determinations has been deposited with the Cambridge Crystallographic Data Centre (see Table S1).

Disorder and Refinement Specifics. The solid-state structure *cis,fac*-[$Re(CO)_3Br(CNAr^{Dipp2})_2$] suffered from positional disorder between the bromide and carbonyl ligands. The disorder did not affect the stereochemistry of the complexes and was adequately modeled and refined with an occupational ration of 0.47/0.53. The solid-state structure of *trans,mer*-[$Re(CO)_3Br(CNAr^{Dipp2})_2$] also suffered from a positional disorder of the three carbonyl ligands and the bromide over all four equatorial sites. This disorder was adequately modeled with a 75/25 occupancy at each site.

Table S1. Crystal data and structure determination parameters

	cis,fac-[$Re(CO)_3Br(CNAr^{Dipp2})_2$]	*trans,mer*-[$Re(CO)_3Br(CNAr^{Dipp2})_2$]	$K[Re(CO)_3(CNAr^{Dipp2})_2]$
Formula	$C_{65}H_{74}BrN_2O_3Re$	$C_{65}H_{74}BrN_2O_3Re$	$C_{65}H_{74}KN_2O_3Re$
M_w	1197.37	1197.37	1156.56
a/Å	20.709(1)	24.097(2)	10.5021(5)
b/Å	10.9734(5)	24.011(2)	12.1274(6)
c/Å	25.496(1)	21.223(3)	25.1217(13)
α	90°	90°	84.635(1)
β	95.441(1)°	108.410(5)°	87.156(2)
γ	90°	90°	66.182(1)
V/ Å^3	5767.8(5)	11651(2)	2914.0(3)
Space group	P 2_1/c	C 2/c	$P\bar{1}$
Z	4	8	2
D_{calc} g/cm^{-3}	1.379	1.365	1.318
μ/mm^{-1}	2.845	2.817	2.202
No. reflect.	34209	148297	21928
No. indep.	10580	12809	10700
R_{int}	0.0479	0.0438	0.0220
No. param.	660	703	665
R_1/wR_2 [I>2σ(I)]	0.0324/ 0.0699	0.026/0.0527	0.0237/0.0545
GOF	1.011	1.079	1.063
CCDC	1990087	1990088	1990089

Figure S1. Ellipsoid representation of *cis*,*fac*-[Re(CO)$_3$Br(CNAr^{Dipp2})$_2$].

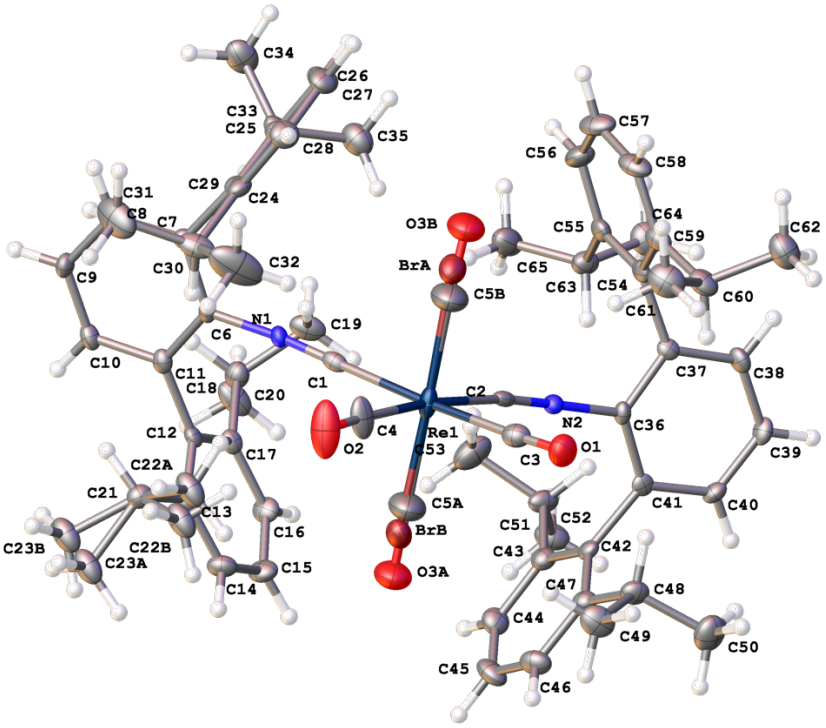

Table S2. Bond lengths (Å) for *cis*,*fac*-[Re(CO)$_3$Br(CNAr^{Dipp2})$_2$].

Re1	C4	1.980(4)	C25	C33	1.508(5)	C9	C10	1.387(5)	C44	C45	1.375(5)
Re1	C5A	1.952(10)	C26	C27	1.371(5)	C10	C11	1.398(4)	C45	C46	1.376(5)
Re1	C5B	1.963(10)	C27	C28	1.372(5)	C11	C12	1.500(5)	C46	C47	1.392(5)
Re1	C3	2.014(4)	C28	C29	1.391(5)	C12	C13	1.400(5)	C47	C48	1.520(5)
Re1	C1	2.072(4)	C29	C30	1.520(5)	C12	C17	1.406(5)	C48	C50	1.524(5)
Re1	C2	2.076(4)	C30	C31	1.512(6)	C13	C14	1.399(5)	C48	C49	1.534(5)
Re1	BrB	2.4693(12)	C30	C32	1.527(6)	C13	C21	1.522(5)	C51	C53	1.524(5)
Re1	BrA	2.4843(10)	C33	C34	1.529(5)	C14	C15	1.376(5)	C51	C52	1.536(5)
C1	N1	1.158(4)	C33	C35	1.532(5)	C15	C16	1.381(5)	C54	C59	1.396(5)
C2	N2	1.155(4)	C36	C37	1.398(4)	C16	C17	1.386(5)	C54	C55	1.407(5)
C3	O1	1.075(4)	C36	C41	1.399(5)	C17	C18	1.523(5)	C55	C56	1.395(5)
C4	O2	1.115(4)	C37	C38	1.395(5)	C18	C20	1.527(5)	C55	C63	1.531(5)
O3A	C5A	1.293(11)	C37	C54	1.503(5)	C18	C19	1.530(5)	C56	C57	1.380(5)
O3B	C5B	1.289(11)	C38	C39	1.384(5)	C21	C22B	1.461(16)	C57	C58	1.367(5)
C6	C11	1.395(5)	C39	C40	1.383(5)	C21	C23B	1.492(12)	C58	C59	1.396(5)
C6	N1	1.405(4)	C40	C41	1.396(4)	C21	C22A	1.529(8)	C59	C60	1.530(5)
C6	C7	1.406(5)	C41	C42	1.500(4)	C21	C23A	1.551(7)	C60	C61	1.533(5)
N2	C36	1.402(4)	C42	C47	1.403(5)	C24	C29	1.408(5)	C60	C62	1.541(5)
C7	C8	1.391(4)	C42	C43	1.410(5)	C24	C25	1.411(5)	C63	C65	1.527(5)
C7	C24	1.494(4)	C43	C44	1.395(5)	C25	C26	1.398(5)	C63	C64	1.531(5)
C8	C9	1.387(5)	C43	C51	1.512(5)						

Table S3. Bond angles (deg) for *cis*,*fac*-[$Re(CO)_3Br(CNAr^{Dipp2})_2$].

C4	Re1	C5A	88.9(6)	C29	C24	C7	120.2(3)
C4	Re1	C5B	92.7(6)	C25	C24	C7	119.1(3)
C4	Re1	C3	88.34(15)	C26	C25	C24	118.0(3)
C5A	Re1	C3	91.7(6)	C26	C25	C33	119.3(3)
C5B	Re1	C3	89.2(6)	C24	C25	C33	122.6(3)
C4	Re1	C1	88.27(14)	C27	C26	C25	121.1(4)
C5A	Re1	C1	92.4(6)	C26	C27	C28	120.6(4)
C5B	Re1	C1	86.8(6)	C27	C28	C29	120.9(4)
C3	Re1	C1	174.62(14)	C28	C29	C24	118.6(3)
C4	Re1	C2	172.97(15)	C28	C29	C30	119.6(3)
C5A	Re1	C2	86.7(6)	C24	C29	C30	121.7(3)
C5B	Re1	C2	91.8(6)	C31	C30	C29	110.6(3)
C3	Re1	C2	86.27(13)	C31	C30	C32	110.0(4)
C1	Re1	C2	97.43(13)	C29	C30	C32	112.6(3)
C4	Re1	BrB	87.78(13)	C25	C33	C34	111.1(3)
C5B	Re1	BrB	178.5(6)	C25	C33	C35	111.1(3)
C3	Re1	BrB	92.24(11)	C34	C33	C35	110.8(3)
C1	Re1	BrB	91.80(9)	C37	C36	C41	123.4(3)
C2	Re1	BrB	87.94(9)	C37	C36	N2	117.8(3)
C4	Re1	BrA	91.87(13)	C41	C36	N2	118.8(3)
C5A	Re1	BrA	178.2(6)	C38	C37	C36	117.0(3)
C3	Re1	BrA	90.00(10)	C38	C37	C54	120.6(3)
C1	Re1	BrA	85.93(9)	C36	C37	C54	122.3(3)
C2	Re1	BrA	92.63(9)	C39	C38	C37	120.8(3)
N1	C1	Re1	171.6(3)	C40	C39	C38	120.7(3)
N2	C2	Re1	168.7(3)	C39	C40	C41	120.8(3)
O1	C3	Re1	176.9(3)	C40	C41	C36	117.0(3)
O2	C4	Re1	177.1(4)	C40	C41	C42	120.3(3)
O3A	C5A	Re1	179.5(18)	C36	C41	C42	122.5(3)
O3B	C5B	Re1	174.1(17)	C47	C42	C43	121.1(3)
C11	C6	N1	118.0(3)	C47	C42	C41	121.3(3)
C11	C6	C7	123.7(3)	C43	C42	C41	117.6(3)
N1	C6	C7	118.2(3)	C44	C43	C42	118.0(3)
C1	N1	C6	173.4(3)	C44	C43	C51	120.0(3)
C2	N2	C36	167.9(3)	C42	C43	C51	121.9(3)
C8	C7	C6	116.4(3)	C45	C44	C43	121.2(3)
C8	C7	C24	121.2(3)	C44	C45	C46	120.2(4)
C6	C7	C24	122.3(3)	C45	C46	C47	121.3(4)
C9	C8	C7	121.6(3)	C46	C47	C42	118.2(3)
C8	C9	C10	120.3(3)	C46	C47	C48	120.8(3)
C9	C10	C11	120.7(3)	C42	C47	C48	120.9(3)
C6	C11	C10	117.2(3)	C47	C48	C50	109.7(3)
C6	C11	C12	120.2(3)	C47	C48	C49	113.1(3)
C10	C11	C12	122.6(3)	C50	C48	C49	110.1(3)
C13	C12	C17	121.3(3)	C43	C51	C53	110.3(3)
C13	C12	C11	119.7(3)	C43	C51	C52	113.5(3)
C17	C12	C11	119.0(3)	C53	C51	C52	110.7(3)
C14	C13	C12	118.0(3)	C59	C54	C55	121.2(3)

C14	C13	C21	119.7(3)	C59	C54	C37	120.5(3)
C12	C13	C21	122.3(3)	C55	C54	C37	118.2(3)
C15	C14	C13	121.3(3)	C56	C55	C54	118.3(3)
C14	C15	C16	119.6(3)	C56	C55	C63	119.6(3)
C15	C16	C17	121.7(3)	C54	C55	C63	122.0(3)
C16	C17	C12	118.0(3)	C57	C56	C55	120.4(4)
C16	C17	C18	120.3(3)	C58	C57	C56	120.9(4)
C12	C17	C18	121.6(3)	C57	C58	C59	120.8(4)
C17	C18	C20	112.9(3)	C58	C59	C54	118.4(4)
C17	C18	C19	111.4(3)	C58	C59	C60	119.9(3)
C20	C18	C19	109.9(3)	C54	C59	C60	121.6(3)
C22B	C21	C23B	115.5(7)	C59	C60	C61	112.8(3)
C22B	C21	C13	113.8(6)	C59	C60	C62	109.6(3)
C23B	C21	C13	109.1(5)	C61	C60	C62	110.5(3)
C13	C21	C22A	111.5(4)	C65	C63	C64	110.2(3)
C13	C21	C23A	111.6(3)	C65	C63	C55	113.3(3)
C22A	C21	C23A	109.7(4)	C64	C63	C55	110.4(3)
C29	C24	C25	120.6(3)				

Table S4. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 x\ 10^3$) for *cis,fac*-[$Re(CO)_3Br(CNAr^{Dipp2})_2$]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Re(1)	7370(1)	7039(1)	7273(1)	22(1)
C(1)	7340(2)	6228(3)	6537(1)	16(1)
C(2)	7512(2)	5463(3)	7719(1)	16(1)
C(3)	7457(2)	7944(3)	7963(2)	23(1)
C(4)	7169(2)	8613(4)	6914(2)	33(1)
BrA	8551(1)	7297(1)	7202(1)	32(1)
O(3A)	5828(4)	6622(8)	7337(3)	53(2)
C(5A)	6443(5)	6791(18)	7314(7)	53(2)
BrB	6192(1)	6754(1)	7306(1)	33(1)
O(3B)	8926(4)	7240(8)	7214(3)	53(2)
C(5B)	8307(5)	7233(19)	7232(8)	53(2)
C(6)	7293(2)	5647(3)	5562(1)	14(1)
N(1)	7341(1)	5915(2)	6103(1)	13(1)
N(2)	7562(1)	4706(3)	8035(1)	14(1)
O(1)	7525(1)	8455(3)	8324(1)	35(1)
O(2)	7032(2)	9500(3)	6722(1)	56(1)
C(7)	7831(2)	5894(3)	5282(1)	14(1)
C(8)	7757(2)	5649(3)	4744(1)	18(1)
C(9)	7181(2)	5193(3)	4498(1)	18(1)
C(10)	6663(2)	4947(3)	4789(1)	18(1)
C(11)	6711(2)	5163(3)	5332(1)	16(1)
C(12)	6175(2)	4858(3)	5667(1)	14(1)
C(13)	5718(2)	5749(3)	5766(1)	18(1)
C(14)	5267(2)	5472(3)	6123(1)	22(1)
C(15)	5264(2)	4354(3)	6367(1)	24(1)

C(16)	5696(2)	3466(3)	6241(1)	21(1)
C(17)	6158(2)	3691(3)	5893(1)	16(1)
C(18)	6633(2)	2698(3)	5768(1)	22(1)
C(19)	7240(2)	2713(3)	6160(2)	28(1)
C(20)	6331(2)	1428(3)	5748(2)	33(1)
C(21)	5695(2)	6987(3)	5495(1)	20(1)
C(22A)	5990(4)	7982(7)	5862(3)	30(1)
C(23A)	4992(3)	7344(6)	5287(3)	30(1)
C(22B)	5716(7)	8016(14)	5860(6)	30(1)
C(23B)	5149(7)	7000(12)	5069(6)	30(1)
C(24)	8460(2)	6349(3)	5545(1)	16(1)
C(25)	8958(2)	5507(3)	5696(1)	19(1)
C(26)	9556(2)	5962(4)	5912(1)	26(1)
C(27)	9655(2)	7189(4)	5981(2)	27(1)
C(28)	9164(2)	8003(4)	5846(1)	26(1)
C(29)	8561(2)	7608(3)	5624(1)	19(1)
C(30)	8029(2)	8534(3)	5474(2)	28(1)
C(31)	8029(2)	8895(4)	4902(2)	51(1)
C(32)	8086(2)	9667(4)	5823(2)	64(2)
C(33)	8864(2)	4148(3)	5643(1)	24(1)
C(34)	9299(2)	3613(4)	5249(2)	35(1)
C(35)	8986(2)	3516(4)	6179(2)	34(1)
C(36)	7651(2)	3992(3)	8492(1)	14(1)
C(37)	8285(2)	3652(3)	8672(1)	14(1)
C(38)	8372(2)	3040(3)	9153(1)	19(1)
C(39)	7847(2)	2751(3)	9427(1)	18(1)
C(40)	7222(2)	3045(3)	9226(1)	17(1)
C(41)	7108(2)	3670(3)	8749(1)	14(1)
C(42)	6427(2)	3878(3)	8509(1)	15(1)
C(43)	6135(2)	2948(3)	8188(1)	20(1)
C(44)	5492(2)	3107(3)	7983(2)	25(1)
C(45)	5151(2)	4137(4)	8091(2)	29(1)
C(46)	5443(2)	5042(3)	8403(2)	26(1)
C(47)	6084(2)	4937(3)	8618(1)	19(1)
C(48)	6395(2)	5922(3)	8977(1)	24(1)
C(49)	6151(2)	7206(3)	8826(2)	32(1)
C(50)	6281(2)	5646(4)	9547(2)	39(1)
C(51)	6508(2)	1836(3)	8038(2)	24(1)
C(52)	6152(2)	631(3)	8116(2)	31(1)
C(53)	6687(2)	1949(4)	7474(2)	42(1)
C(54)	8849(2)	3872(3)	8354(1)	17(1)
C(55)	8981(2)	2998(3)	7975(1)	20(1)
C(56)	9526(2)	3165(4)	7701(2)	29(1)
C(57)	9920(2)	4169(4)	7800(2)	33(1)
C(58)	9780(2)	5027(4)	8161(2)	28(1)
C(59)	9244(2)	4894(3)	8448(1)	21(1)
C(60)	9114(2)	5835(3)	8869(2)	25(1)
C(61)	9121(2)	7148(3)	8664(2)	37(1)
C(62)	9612(2)	5677(4)	9352(2)	37(1)
C(63)	8572(2)	1842(3)	7882(1)	23(1)
C(64)	8876(2)	788(3)	8212(2)	32(1)
C(65)	8465(2)	1473(4)	7303(2)	35(1)

Figure S2. Ellipsoid representation of *trans,mer*-[Re(CO)$_3$Br(CNAr^{Dipp2})$_2$].

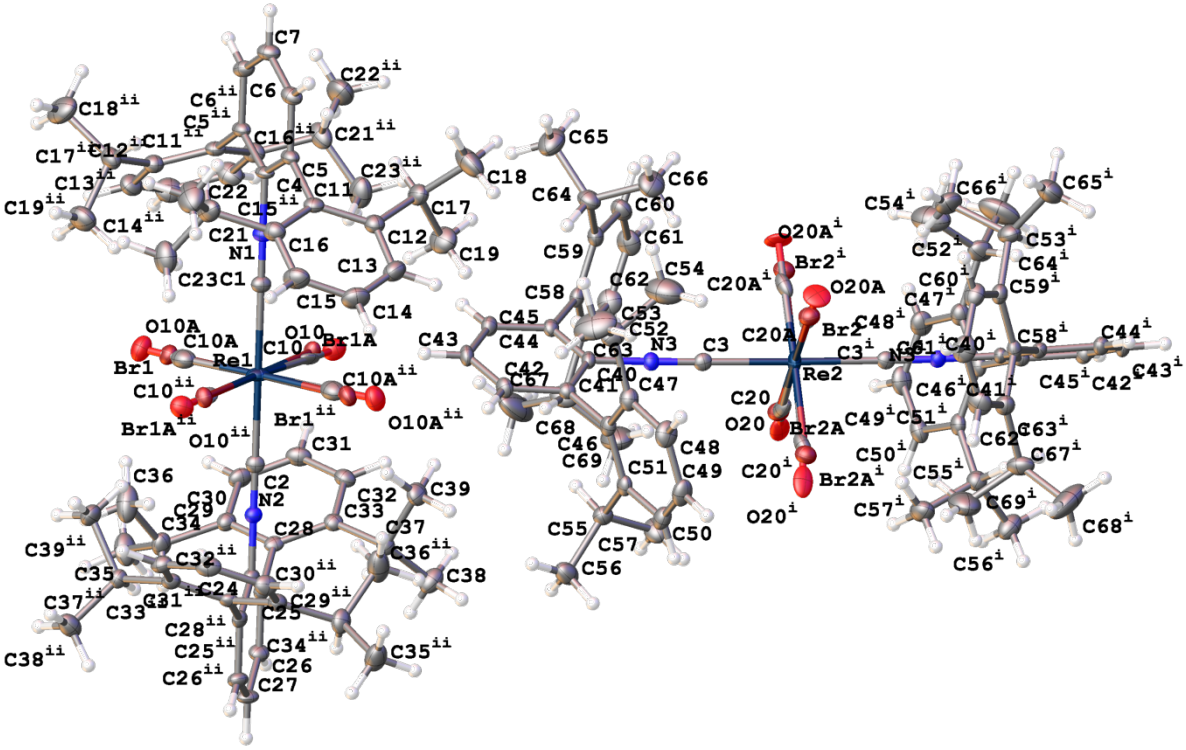

Table S5. Bond lengths (Å) for *trans,mer*-[Re(CO)$_3$Br(CNAr^{Dipp2})$_2$].

Re2	Br2A^{1}	2.454(3)	C59	C64	1.518(4)
Re2	Br2A	2.454(3)	C44	C43	1.392(4)
Re2	Br2^{1}	2.507(2)	C6	C7	1.393(3)
Re2	Br2	2.506(2)	C6	C5	1.392(3)
Re2	C3	2.044(2)	C32	C33	1.401(4)
Re2	C3^{1}	2.044(2)	C32	C31	1.384(4)
Re2	C20A^{1}	1.970(6)	C4	C5^{2}	1.406(3)
Re2	C20A	1.970(6)	C4	C5	1.406(3)
Re2	C20^{1}	2.169(10)	C51	C50	1.402(4)
Re2	C20	2.169(10)	C51	C55	1.525(4)
Re1	Br1A	2.443(3)	C30	C31	1.386(4)
Re1	Br1A^{2}	2.443(3)	C30	C29	1.397(4)
Re1	Br1^{2}	2.495(2)	C63	C62	1.395(4)
Re1	Br1	2.495(2)	C63	C67	1.525(4)
Re1	C1	2.061(4)	C47	C48	1.399(4)
Re1	C2	2.050(4)	C47	C52	1.524(4)
Re1	C10A	2.012(8)	C50	C49	1.379(4)
Re1	C10A^{2}	2.012(8)	C42	C41	1.399(3)
Re1	C10	2.054(10)	C42	C43	1.381(4)
Re1	C10^{2}	2.054(10)	C33	C37	1.524(4)
N2	C24	1.405(4)	C16	C15	1.390(4)

N2	C2	1.157(5)	C16	C21	1.524(4)
N3	C3	1.159(3)	C48	C49	1.381(4)
N3	C40	1.402(3)	C34	C29	1.526(4)
N1	C1	1.147(5)	C34	C35	1.521(4)
N1	C4	1.409(4)	C34	C36	1.528(4)
C24	C25	1.397(3)	C60	C61	1.383(4)
C24	C25[2]	1.397(3)	C62	C61	1.379(4)
C28	C25	1.497(4)	C64	C66	1.534(4)
C28	C33	1.402(4)	C64	C65	1.531(4)
C28	C29	1.416(4)	C55	C57	1.526(4)
C58	C45	1.493(4)	C55	C56	1.533(4)
C58	C59	1.409(4)	C13	C14	1.384(4)
C58	C63	1.414(4)	C14	C15	1.382(4)
C11	C12	1.404(4)	C17	C19	1.525(4)
C11	C16	1.415(4)	C17	C18	1.530(5)
C11	C5	1.496(4)	C67	C69	1.509(5)
C25	C26	1.392(3)	C67	C68	1.522(5)
C45	C40	1.411(3)	C52	C53	1.519(5)
C45	C44	1.393(3)	C52	C54	1.531(5)
C26	C27	1.396(3)	C37	C39	1.530(4)
C46	C51	1.408(4)	C37	C38	1.530(4)
C46	C47	1.412(4)	C21	C23	1.531(5)
C46	C41	1.499(3)	C21	C22	1.533(5)
C40	C41	1.394(3)	O10	C10	1.089(10)
C12	C13	1.396(4)	O20	C20	0.922(11)
C12	C17	1.519(4)	O10A	C10A	1.147(8)
C59	C60	1.396(4)	O20A	C20A	1.223(6)

[1]2-x,y,3/2-z; [2]1-x,y,3/2-z

Table S6. Bond angles (°) for *trans,mer*-[$Re(CO)_3Br(CNAr^{Dipp2})_2$].

Br2A[1]	Re2	Br2A	96.44(18)	C44	C45	C40	117.0(2)
Br2A[1]	Re2	Br2[1]	176.62(8)	C25	C26	C27	120.5(3)
Br2A	Re2	Br2[1]	80.36(11)	C51	C46	C47	121.4(2)
C3[1]	Re2	Br2A	90.85(12)	C51	C46	C41	119.2(2)
C3[1]	Re2	Br2A[1]	89.70(12)	C47	C46	C41	119.4(2)
C3	Re2	Br2A	89.70(12)	N3	C40	C45	118.1(2)
C3	Re2	Br2A[1]	90.85(12)	C41	C40	N3	118.4(2)
C3	Re2	Br2[1]	90.21(8)	C41	C40	C45	123.5(2)
C3[1]	Re2	Br2[1]	89.27(8)	C11	C12	C17	122.1(2)
C3[1]	Re2	Br2	90.22(8)	C13	C12	C11	118.5(3)
C3	Re2	Br2	89.27(8)	C13	C12	C17	119.5(3)

C3[1]	Re2	C3	179.18(15)	C58	C59	C64	121.9(2)
C3[1]	Re2	C20	89.9(3)	C60	C59	C58	118.3(3)
C3[1]	Re2	C20[1]	90.6(3)	C60	C59	C64	119.8(3)
C3	Re2	C20[1]	89.9(3)	C43	C44	C45	120.6(2)
C3	Re2	C20	90.6(3)	C5	C6	C7	120.9(3)
C20A	Re2	Br2A[1]	85.23(14)	C31	C32	C33	120.6(3)
C20A[1]	Re2	Br2A[1]	178.0(2)	C5	C4	N1	118.30(16)
C20A[1]	Re2	Br2A	85.23(14)	C5[2]	C4	N1	118.30(16)
C20A	Re2	Br2A	178.0(2)	C5	C4	C5[2]	123.4(3)
C20A	Re2	Br2[1]	97.95(15)	C46	C51	C55	122.6(2)
C20A[1]	Re2	Br2[1]	5.31(18)	C50	C51	C46	118.2(3)
C20A[1]	Re2	C3[1]	91.33(18)	C50	C51	C55	119.3(2)
C20A	Re2	C3	91.33(18)	C31	C30	C29	121.2(3)
C20A	Re2	C3[1]	88.11(18)	C58	C63	C67	121.8(2)
C20A[1]	Re2	C3	88.10(18)	C62	C63	C58	118.2(3)
C20A[1]	Re2	C20A	93.1(3)	C62	C63	C67	120.0(3)
C20A[1]	Re2	C20[1]	178.0(3)	C46	C47	C52	121.4(2)
C20A	Re2	C20[1]	86.8(4)	C48	C47	C46	117.8(3)
C20	Re2	Br2	175.3(3)	C48	C47	C52	120.7(3)
C20[1]	Re2	Br2	81.9(3)	C49	C50	C51	120.9(3)
C20[1]	Re2	C20	93.4(7)	C43	C42	C41	120.8(2)
Br1A	Re1	Br1A[2]	179.7(2)	C28	C33	C37	122.3(2)
Br1A	Re1	Br1[2]	98.24(11)	C32	C33	C28	118.6(2)
Br1A[2]	Re1	Br1[2]	81.77(11)	C32	C33	C37	119.2(2)
C1	Re1	Br1A[2]	89.85(10)	C26[2]	C27	C26	120.4(3)
C1	Re1	Br1A	89.85(10)	C40	C41	C46	122.0(2)
C1	Re1	Br1	90.43(9)	C40	C41	C42	117.1(2)
C1	Re1	Br1[2]	90.43(9)	C42	C41	C46	120.9(2)
C2	Re1	Br1A[2]	90.15(10)	C11	C16	C21	121.5(3)
C2	Re1	Br1A	90.15(10)	C15	C16	C11	118.1(3)
C2	Re1	Br1[2]	89.57(9)	C15	C16	C21	120.4(3)
C2	Re1	Br1	89.57(9)	C42	C43	C44	121.0(2)
C2	Re1	C1	180.0	C49	C48	C47	121.3(3)
C2	Re1	C10[2]	88.1(4)	C29	C34	C36	111.0(3)
C2	Re1	C10	88.1(4)	C35	C34	C29	114.0(2)
C10A	Re1	Br1A[2]	95.8(4)	C35	C34	C36	109.7(3)
C10A[2]	Re1	Br1A[2]	84.2(4)	C32	C31	C30	120.4(3)
C10A[2]	Re1	Br1A	95.8(4)	C28	C29	C34	121.0(2)
C10A	Re1	Br1A	84.2(4)	C30	C29	C28	117.9(3)
C10A[2]	Re1	Br1[2]	2.5(4)	C30	C29	C34	121.1(2)
C10A	Re1	Br1[2]	177.5(4)	C6	C7	C6[2]	120.6(4)
C10A[2]	Re1	C1	90.1(4)	C6	C5	C11	122.1(2)
C10A	Re1	C1	90.1(4)	C6	C5	C4	117.1(3)
C10A[2]	Re1	C2	89.9(4)	C4	C5	C11	120.8(2)
C10A	Re1	C2	89.9(4)	C61	C60	C59	121.0(3)

C10A[2]	Re1	C10A	179.7(9)	C61	C62	C63	121.2(3)
C10A	Re1	C10[2]	92.1(5)	C59	C64	C66	110.8(2)
C10A[2]	Re1	C10[2]	87.9(5)	C59	C64	C65	111.6(3)
C10	Re1	Br1	85.4(4)	C65	C64	C66	110.5(3)
C10[2]	Re1	Br1	94.5(4)	C50	C49	C48	120.4(3)
C10	Re1	C1	91.9(4)	C51	C55	C57	111.4(2)
C10[2]	Re1	C1	91.9(4)	C51	C55	C56	111.9(2)
C10[2]	Re1	C10	176.3(8)	C57	C55	C56	109.3(3)
C2	N2	C24	180.0	C14	C13	C12	120.7(3)
C3	N3	C40	178.1(3)	C15	C14	C13	120.4(3)
C1	N1	C4	180.0	C12	C17	C19	112.1(3)
N3	C3	Re2	179.5(2)	C12	C17	C18	110.7(3)
N1	C1	Re1	180.0	C19	C17	C18	111.2(3)
C25	C24	N2	118.32(16)	C14	C15	C16	121.2(3)
C25[2]	C24	N2	118.33(16)	C62	C61	C60	120.3(3)
C25[2]	C24	C25	123.3(3)	C69	C67	C63	111.6(3)
C33	C28	C25	119.1(2)	C69	C67	C68	110.3(3)
C33	C28	C29	121.3(2)	C68	C67	C63	112.7(3)
C29	C28	C25	119.6(2)	C47	C52	C54	110.9(3)
C59	C58	C45	119.7(2)	C53	C52	C47	113.9(3)
C59	C58	C63	121.0(2)	C53	C52	C54	110.3(3)
C63	C58	C45	119.3(2)	C33	C37	C39	112.0(2)
N2	C2	Re1	180.0	C33	C37	C38	111.1(2)
C12	C11	C16	121.1(3)	C38	C37	C39	110.7(2)
C12	C11	C5	119.7(2)	C16	C21	C23	110.8(3)
C16	C11	C5	119.1(2)	C16	C21	C22	112.6(3)
C24	C25	C28	121.3(2)	C23	C21	C22	110.6(3)
C26	C25	C24	117.6(3)	O10A	C10A	Re1	178.4(14)
C26	C25	C28	121.2(2)	O20A	C20A	Re2	176.2(5)
C40	C45	C58	120.8(2)	O20	C20	Re2	175.5(12)
C44	C45	C58	122.2(2)	O10	C10	Re1	178.0(11)

[1]2-x,y,3/2-z; [2]1-x,y,3/2-z

Table 7. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for *trans,mer*-[$Re(CNAr^{Dipp2})_2(CO)_3Br$]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Re2	10000	5645.4(2)	7500	19.91(4)
Re1	5000	5616.2(2)	7500	20.78(4)
Br2A	9763.8(17)	4964.3(15)	6591.3(15)	22.4(3)

Br1A	5393.8(17)	5618.9(18)	6571.2(14)	17.0(5)
Br1	4053.6(12)	5608.4(16)	6575.2(13)	21.5(5)
Br2	10233.3(8)	6296.2(8)	8472.1(9)	22.4(3)
N2	5000	4280.7(12)	7500	15.5(6)
N3	8656.2(9)	5659.2(9)	7443.5(10)	15.7(4)
N1	5000	6952.5(12)	7500	17.4(6)
C3	9142.5(11)	5651.5(11)	7464.3(12)	16.0(5)
C1	5000	6474.8(15)	7500	17.5(7)
C24	5000	3695.6(14)	7500	14.5(7)
C28	5071.2(11)	3735.1(10)	6340.1(12)	15.8(5)
C58	7810.7(11)	6008.5(11)	6245.3(13)	16.7(5)
C2	5000	4762.7(15)	7500	16.2(7)
C11	5604.2(12)	7496.8(10)	8710.3(13)	18.4(5)
C25	5033.1(11)	3419.5(11)	6933.5(12)	15.7(5)
C45	7645.9(11)	5860.2(10)	6846.1(13)	15.8(5)
C26	5032.3(12)	2839.6(11)	6941.8(13)	19.7(5)
C46	8406.8(11)	5318.3(11)	8614.3(13)	17.8(5)
C40	8072.7(10)	5682.4(10)	7435.0(13)	15.2(5)
C12	6188.9(12)	7334.5(11)	8835.4(14)	21.8(6)
C59	7955.1(11)	6563.5(11)	6147.6(14)	20.0(5)
C44	7070.9(11)	5889.2(11)	6854.4(13)	18.2(5)
C6	5292.4(12)	8396.6(11)	8079.8(14)	20.6(6)
C32	5648.8(12)	4220.0(11)	5771.9(14)	21.4(6)
C4	5000	7539.3(14)	7500	16.3(7)
C51	8582.2(11)	4756.8(11)	8648.8(13)	18.5(5)
C30	4611.8(13)	4121.0(11)	5251.5(14)	23.3(6)
C63	7831.2(12)	5585.6(12)	5789.7(13)	21.8(5)
C47	8652.9(12)	5690.3(12)	9144.0(13)	22.4(6)
C50	9008.2(12)	4572.8(13)	9228.5(14)	24.4(6)
C42	7358.9(11)	5558.8(11)	7985.6(13)	19.1(5)
C33	5617.6(12)	3929.1(10)	6331.9(13)	18.0(5)
C27	5000	2550.9(15)	7500	20.7(8)
C41	7943.7(11)	5522.9(10)	8005.0(12)	15.6(5)
C16	5293.1(13)	7352.9(12)	9151.9(14)	24.1(6)
C43	6932.6(11)	5742.5(11)	7421.7(14)	19.4(5)
C48	9074.3(13)	5482.0(13)	9711.1(14)	28.3(7)
C34	3962.0(12)	3634.5(13)	5822.0(14)	25.5(6)
C31	5150.9(13)	4310.6(11)	5236.9(13)	24.3(6)
C29	4557.7(12)	3829.4(11)	5798.5(13)	19.7(5)
C7	5000	8684.0(16)	7500	22.9(8)
C5	5298.0(12)	7816.9(10)	8093.7(13)	17.8(5)
C60	8125.7(13)	6685.0(13)	5592.2(14)	26.0(6)
C62	8005.5(13)	5731.0(13)	5244.0(14)	28.8(6)
C35	3552.2(14)	3437.9(16)	5156.0(17)	38.5(8)
C64	7936.8(13)	7024.2(12)	6630.7(15)	27.0(6)

C49	9245.8(13)	4930.7(14)	9752.9(14)	28.1(6)
C55	8326.6(12)	4346.1(12)	8083.5(13)	21.8(5)
C13	6453.5(13)	7010.5(12)	9396.4(15)	28.3(6)
C14	6147.3(15)	6856.6(14)	9821.7(15)	33.6(7)
C17	6538.5(13)	7501.4(12)	8381.9(16)	26.6(6)
C15	5575.5(14)	7027.9(13)	9701.5(16)	31.1(7)
C61	8154.4(14)	6272.0(14)	5149.0(15)	30.3(7)
C67	7678.2(14)	4982.4(12)	5888.1(15)	29.4(7)
C52	8479.5(14)	6303.2(13)	9096.9(15)	30.0(7)
C37	6176.2(11)	3831.2(11)	6908.3(13)	19.6(5)
C21	4659.7(14)	7531.5(13)	9022.7(16)	31.4(7)
C36	3663.2(15)	4087.9(17)	6104.3(18)	44.2(9)
C39	6483.7(12)	4377.7(13)	7185.9(15)	27.6(6)
C38	6592.1(13)	3440.6(13)	6705.9(15)	30.2(7)
C23	4243.5(15)	7039.0(16)	8780.2(17)	39.8(8)
C57	8794.6(14)	4129.7(13)	7800.5(17)	33.4(7)
C66	8553.3(15)	7245.7(14)	6986.7(18)	38.6(8)
C56	8030.0(14)	3851.6(13)	8303.5(16)	32.1(7)
C22	4559.1(17)	7803.4(16)	9631(2)	48.6(10)
C19	6751.9(16)	6996.8(14)	8087.9(18)	39.7(8)
C69	8201.2(19)	4604.1(16)	6005(2)	59.3(12)
C53	8383(2)	6531.6(17)	9722(2)	59.3(12)
C68	7168(2)	4765.3(19)	5316(2)	73.1(15)
C65	7531.0(16)	7499.4(15)	6283.9(19)	42.6(9)
C18	7047.8(17)	7881.7(16)	8747(2)	48.9(10)
C54	8927(2)	6660.2(17)	8903(2)	61.2(12)
O10	5573.9(15)	5580.5(14)	6361.0(17)	25.8(7)
O20	9760.0(15)	4752.8(16)	6398.0(18)	31.7(9)
O10A	3775.4(16)	5625.4(19)	6372(2)	29.6(9)
O20A	10320.5(14)	6535.6(14)	8676.5(16)	29.1(7)
C10A	4219(5)	5614(6)	6783(5)	30(2)
C20A	10200(3)	6209(3)	8210(3)	23.8(13)
C20	9811(5)	5026(5)	6717(5)	23.8(13)
C10	5384(6)	5588(6)	6763(4)	20(2)

Figure S3. Ellipsoid representation of K[Re(CO)$_3$(CNAr^{Dipp2})$_2$].

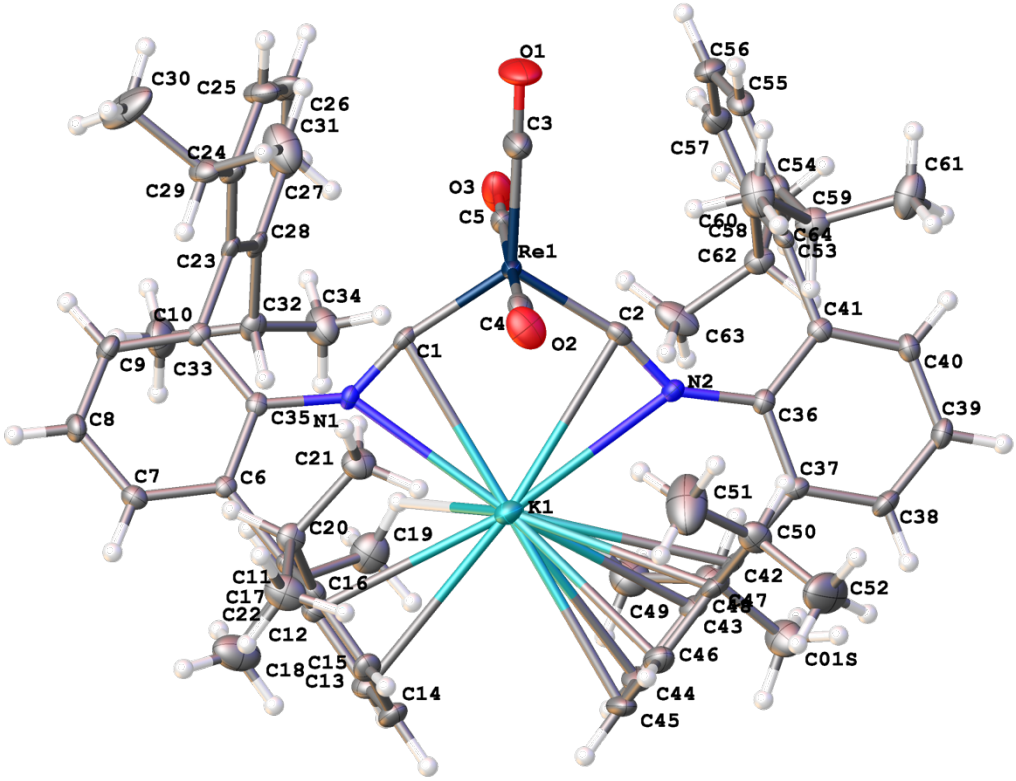

Table S8. Bond lengths and distances (Å) for K[Re(CO)$_3$(CNAr^{Dipp2})$_2$].

Re1	K1	3.6835(6)	C20	C22	1.531(3)
Re1	C1	1.936(2)	C23	C24	1.398(4)
Re1	C2	1.942(2)	C23	C28	1.416(3)
Re1	C3	1.970(3)	C24	C25	1.394(4)
Re1	C4	1.975(3)	C24	C29	1.527(4)
Re1	C5	1.986(3)	C25	C26	1.378(4)
K1	N1	2.9704(19)	C26	C27	1.379(4)
K1	N2	3.121(2)	C27	C28	1.393(4)
K1	C1	3.063(2)	C28	C32	1.523(4)
K1	C2	3.173(2)	C29	C30	1.524(4)
K1	C12	3.340(2)	C29	C31	1.521(4)
K1	C13	3.409(3)	C32	C33	1.529(4)
K1	C42	3.493(2)	C32	C34	1.527(4)
K1	C43	3.488(3)	C36	C37	1.398(3)
K1	C44	3.420(3)	C36	C41	1.410(3)
K1	C45	3.377(3)	C37	C38	1.396(3)
K1	C46	3.349(3)	C37	C42	1.499(3)
K1	C47	3.400(2)	C38	C39	1.387(4)
O1	C3	1.157(3)	C39	C40	1.383(4)
O2	C4	1.152(3)	C40	C41	1.395(3)
O3	C5	1.151(3)	C41	C53	1.495(3)

N1	C1	1.227(3)	C42	C43	1.398(4)
N1	C35	1.416(3)	C42	C47	1.407(4)
N2	C2	1.218(3)	C43	C44	1.408(4)
N2	C36	1.403(3)	C43	C48	1.518(4)
C01S	C48	1.540(4)	C44	C45	1.386(4)
C6	C7	1.392(3)	C45	C46	1.389(4)
C6	C11	1.504(3)	C46	C47	1.395(4)
C6	C35	1.400(3)	C47	C50	1.523(4)
C7	C8	1.392(3)	C48	C49	1.532(4)
C8	C9	1.384(3)	C50	C51	1.510(4)
C9	C10	1.399(3)	C50	C52	1.505(4)
C10	C23	1.499(3)	C53	C54	1.404(4)
C10	C35	1.407(3)	C53	C58	1.407(3)
C11	C12	1.406(3)	C54	C55	1.395(4)
C11	C16	1.410(3)	C54	C59	1.517(4)
C12	C13	1.402(4)	C55	C56	1.379(4)
C12	C17	1.526(3)	C56	C57	1.379(4)
C13	C14	1.387(4)	C57	C58	1.397(4)
C14	C15	1.384(4)	C58	C62	1.520(4)
C15	C16	1.393(3)	C59	C60	1.534(4)
C16	C20	1.527(4)	C59	C61	1.528(4)
C17	C18	1.518(4)	C62	C63	1.532(4)
C17	C19	1.548(4)	C62	C64	1.526(4)
C20	C21	1.531(4)			

Table S9. Bond angles (°) for $K[Re(CO)_3(CNAr^{Dipp2})_2]$.

Re1	K1	3.6835(6)	C20	C22	1.531(3)
Re1	C1	1.936(2)	C23	C24	1.398(4)
Re1	C2	1.942(2)	C23	C28	1.416(3)
Re1	C3	1.970(3)	C24	C25	1.394(4)
Re1	C4	1.975(3)	C24	C29	1.527(4)
Re1	C5	1.986(3)	C25	C26	1.378(4)
K1	N1	2.9704(19)	C26	C27	1.379(4)
K1	N2	3.121(2)	C27	C28	1.393(4)
K1	C1	3.063(2)	C28	C32	1.523(4)
K1	C2	3.173(2)	C29	C30	1.524(4)
K1	C12	3.340(2)	C29	C31	1.521(4)
K1	C13	3.409(3)	C32	C33	1.529(4)
K1	C42	3.493(2)	C32	C34	1.527(4)
K1	C43	3.488(3)	C36	C37	1.398(3)
K1	C44	3.420(3)	C36	C41	1.410(3)
K1	C45	3.377(3)	C37	C38	1.396(3)

K1	C46	3.349(3)	C37	C42	1.499(3)
K1	C47	3.400(2)	C38	C39	1.387(4)
O1	C3	1.157(3)	C39	C40	1.383(4)
O2	C4	1.152(3)	C40	C41	1.395(3)
O3	C5	1.151(3)	C41	C53	1.495(3)
N1	C1	1.227(3)	C42	C43	1.398(4)
N1	C35	1.416(3)	C42	C47	1.407(4)
N2	C2	1.218(3)	C43	C44	1.408(4)
N2	C36	1.403(3)	C43	C48	1.518(4)
C01S	C48	1.540(4)	C44	C45	1.386(4)
C6	C7	1.392(3)	C45	C46	1.389(4)
C6	C11	1.504(3)	C46	C47	1.395(4)
C6	C35	1.400(3)	C47	C50	1.523(4)
C7	C8	1.392(3)	C48	C49	1.532(4)
C8	C9	1.384(3)	C50	C51	1.510(4)
C9	C10	1.399(3)	C50	C52	1.505(4)
C10	C23	1.499(3)	C53	C54	1.404(4)
C10	C35	1.407(3)	C53	C58	1.407(3)
C11	C12	1.406(3)	C54	C55	1.395(4)
C11	C16	1.410(3)	C54	C59	1.517(4)
C12	C13	1.402(4)	C55	C56	1.379(4)
C12	C17	1.526(3)	C56	C57	1.379(4)
C13	C14	1.387(4)	C57	C58	1.397(4)
C14	C15	1.384(4)	C58	C62	1.520(4)
C15	C16	1.393(3)	C59	C60	1.534(4)
C16	C20	1.527(4)	C59	C61	1.528(4)
C17	C18	1.518(4)	C62	C63	1.532(4)
C17	C19	1.548(4)	C62	C64	1.526(4)
C20	C21	1.531(4)			

Table S10. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 x\ 10^3$) for $K[Re(CO)_3(CNAr^{Dipp2})_2]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	
Re1	5650.92(11)	8729.64(9)	7443.44(4)	15.26(4)
K1	8257.2(6)	5601.4(5)	7393.8(2)	23.29(13)
O1	2923(2)	11094(2)	7383.3(9)	46.1(6)
O2	3981(2)	7395(2)	6998.1(8)	35.3(5)
O3	7085(2)	10271(2)	7887.0(8)	36.9(5)
N1	8008(2)	7630.7(18)	6588.0(7)	12.5(4)
N2	6611(2)	6759.9(18)	8409.4(8)	14.5(4)
C1	7042(3)	8201(2)	6881.4(9)	13.5(5)

C01S	10818(3)	3722(3)	9471.6(11)	33.9(7)
C2	6099(3)	7623(2)	8083.6(10)	15.6(5)
C3	3931(3)	10219(3)	7409.2(11)	29.0(7)
C4	4610(3)	7876(2)	7160.9(10)	22.2(6)
C5	6583(3)	9688(2)	7722.6(10)	22.9(6)
C6	9054(2)	6752(2)	5777.7(9)	11.7(5)
C7	9453(3)	6863(2)	5245.4(9)	15.4(5)
C8	9233(3)	7993(2)	4989.7(9)	17.6(5)
C9	8641(3)	9012(2)	5271.7(9)	16.6(5)
C10	8198(3)	8948(2)	5803.7(9)	12.7(5)
C11	9418(3)	5519(2)	6062.9(9)	12.9(5)
C12	10592(3)	5029(2)	6393.0(9)	15.6(5)
C13	10976(3)	3851(2)	6633.9(10)	20.1(6)
C14	10212(3)	3181(2)	6551.4(10)	21.9(6)
C15	9041(3)	3683(2)	6234.8(10)	19.6(6)
C16	8623(3)	4848(2)	5986.8(9)	15.5(5)
C17	11462(3)	5731(2)	6500.1(10)	19.6(6)
C18	12970(3)	5098(3)	6324.4(15)	40.4(8)
C19	11384(3)	5993(3)	7094.7(12)	34.2(7)
C20	7283(3)	5408(2)	5665.3(10)	18.5(5)
C21	6082(3)	6136(3)	6029.5(11)	25.0(6)
C22	6912(3)	4494(3)	5398.7(12)	30.5(7)
C23	7598(3)	10067(2)	6100.6(9)	14.5(5)
C24	6244(3)	10918(2)	5998.5(10)	18.7(6)
C25	5718(3)	11953(2)	6278.9(11)	27.5(7)
C26	6524(3)	12157(2)	6642.5(11)	29.8(7)
C27	7864(3)	11321(2)	6739.8(10)	23.4(6)
C28	8432(3)	10266(2)	6475.5(9)	16.3(5)
C29	5294(3)	10760(2)	5599.2(10)	21.7(6)
C30	4880(4)	11785(3)	5157.3(13)	49.7(10)
C31	4023(3)	10647(4)	5873.9(12)	42.8(9)
C32	9922(3)	9367(2)	6581.7(10)	17.9(5)
C33	10928(3)	9618(3)	6176.9(12)	34.9(7)
C34	10398(3)	9345(3)	7148.6(11)	31.1(7)
C35	8394(2)	7799(2)	6048.5(9)	12.0(5)
C36	6467(3)	6375(2)	8944.6(9)	13.4(5)
C37	7164(3)	5140(2)	9090.6(9)	15.0(5)
C38	7057(3)	4705(2)	9618.2(10)	18.7(5)
C39	6299(3)	5491(2)	9996.0(10)	18.2(5)
C40	5648(3)	6716(2)	9850.4(9)	16.5(5)
C41	5705(3)	7187(2)	9325.7(9)	13.9(5)
C42	8023(3)	4320(2)	8679.3(9)	16.6(5)
C43	9445(3)	4062(2)	8634.3(10)	20.2(6)
C44	10242(3)	3251(2)	8259.9(11)	25.2(6)

C45	9632(3)	2724(2)	7944.9(11)	26.8(6)
C46	8208(3)	3023(2)	7981.8(11)	24.7(6)
C47	7382(3)	3833(2)	8344.4(10)	19.9(6)
C48	10121(3)	4612(3)	8990.0(11)	24.5(6)
C49	11157(3)	5052(3)	8690.2(13)	35.4(7)
C50	5824(3)	4152(3)	8383.9(11)	24.7(6)
C51	5103(4)	4618(4)	7853.7(15)	62.9(12)
C52	5557(4)	3091(3)	8638.4(16)	49.7(10)
C53	5008(3)	8512(2)	9166.8(9)	13.6(5)
C54	3670(3)	8987(2)	8948.5(9)	16.9(5)
C55	3063(3)	10218(2)	8784.5(10)	20.8(6)
C56	3775(3)	10941(2)	8833.8(11)	25.4(6)
C57	5085(3)	10469(2)	9053.2(10)	22.2(6)
C58	5736(3)	9245(2)	9226.1(9)	16.6(5)
C59	2888(3)	8188(3)	8905.9(10)	22.1(6)
C60	1982(3)	8520(3)	8407.2(11)	34.2(7)
C61	2006(3)	8195(3)	9409.2(11)	33.6(7)
C62	7194(3)	8726(2)	9453.9(10)	19.2(6)
C63	8315(3)	8263(3)	9019.3(12)	30.9(7)
C64	7505(3)	9606(3)	9767.2(11)	28.2(7)

Computational Studies

Computational Details. Density Functional Theory (DFT) calculations were carried out on the truncated model complex $[Re(CO)_3(CNMes)_2]^-$ (Mes = 2,4,6-$Me_3C_6H_3$) using the ORCA computational suite 4.0.0. Geometry optimizations were performed using the B3LYP functional[6-10] along with the all-electron Ahlrichs triple-zeta basis sets def2-TZVP (standard)[11] and def2-TZVP/J (auxiliary).[12] The resolution of identity (RI) approximation was employed.[13] Relativistic effects were included by use of the zeroth order regular approximation (ZORA).[13-15] The input geometry for $[Re(CO)_3(CNMes)_2]^-$ was based on the crystallographic atomic coordinates $KRe(CO)_3(CNAr^{Dipp2})_2$. Visualization of optimized structures and rendering of molecular orbitals for the text was performed using the program Chemcraft.[16]

Input file for $[Re(CO)_3(CNArMes)_2]^-$

```
# ReMesAnion opt-freq
%pal nprocs 8 end
! RKS Opt B3LYP ZORA ZORA-def2-TZVP SARC/J KeepDens VerySlowConv TightSCF
%basis
NewGTO Re "SARC-ZORA-TZVP" end
end
%SCF
MaxIter 3000
end

%output
Print[ P_Basis ] 2
Print[ P_MOs ] 1
end

* xyz -1 1
Re     11.137690   11.186674   18.615593
O      13.454884   12.985943   19.725015
O       9.423282   13.797744   18.465285
O       8.674350    9.615075   17.502168
N      11.301756    9.196256   21.031513
N      12.968289    9.794821   16.476277
C      12.620763   12.306299   19.313859
C      10.056106   12.831087   18.530060
C       9.591281   10.182675   17.909323
C      12.269708   10.486843   17.210057
C      13.388897    9.872818   15.127013
C      13.535507    8.656570   14.449505
C      13.942578    8.672377   13.118748
H      14.023257    7.855160   12.641842
C      14.233059    9.874457   12.479005
C      14.145534   11.061880   13.184273
H      14.384061   11.874211   12.753484
C      13.715259   11.098197   14.514780
C      11.146124   10.088081   20.216452
C      11.028733    8.877195   22.370023
C      11.174094    7.536472   22.735162
C      10.914446    7.160294   24.054665
H      10.986946    6.247140   24.307261
C      10.550417    8.108540   24.999525
C      10.448518    9.438249   24.635386
H      10.220315   10.083512   25.294137
C      10.673648    9.854952   23.323136
C      10.260565    7.681033   26.450326
H       9.185036    7.561707   26.623840
H      10.741316    6.725340   26.688313
H      10.630038    8.423746   27.166550
C      14.649024    9.882544   10.996269
H      15.739567    9.875733   10.887741
H      14.259247    9.005161   10.467705
H      14.271594   10.773027   10.480811
C      13.250992    7.322916   15.165059
H      12.231656    6.972907   14.966170
H      13.940087    6.537591   14.834122
H      13.360075    7.421586   16.251095
C      13.602652   12.428959   15.281586
H      12.562496   12.769282   15.339584
H      13.975616   12.331146   16.307471
```

H	14.182314	13.220866	14.793751
C	11.614587	6.487970	21.696794
H	12.665991	6.209775	21.831941
H	11.017951	5.572136	21.776678
H	11.502219	6.866986	20.674625
C	10.538686	11.337007	22.927031
H	11.467103	11.718592	22.487096
H	9.740364	11.482027	22.190310
H	10.303685	11.962419	23.795790

*

Optimized Cartesian coordinates for $[Re(CO)_3(CNArMes)_2]^-$

Coordinates from ORCA-job ReMesAnion

Re	10.95746633672938	9.97150928580992	18.43715105287129
O	11.94181701414800	12.87668406363025	19.11679572919392
O	8.07209821988973	10.78656108937099	17.66487956827631
O	10.57560670521160	6.89981217577903	17.90148814481085
N	11.15626034008469	9.29215252996317	21.53804316613507
N	12.92406791344692	10.01475472620240	15.93749659198777
C	11.56031059942875	11.81386959382907	18.86351101904793
C	9.15496316613736	10.47995704199572	17.95744569822184
C	10.69776832523178	8.03429826219309	18.09559261073906
C	12.15355860061937	10.01671957209036	16.85779585639620
C	13.42460227239670	10.14323049001214	14.67879817195421
C	13.44745683409090	9.02580289853657	13.81325158736180
C	13.99975686870905	9.17555914341082	12.54727173798308
H	14.00897399963964	8.31543638203603	11.88366141799032
C	14.53537686774880	10.38500520888913	12.10253972531092
C	14.49944726177279	11.47006175423237	12.97746251244718
H	14.90415587165750	12.42448267795526	12.65425474907235
C	13.95933332279795	11.38034721074419	14.25525390195008
C	11.05186743974062	9.55130993718412	20.37337016585377
C	10.94490718234626	9.02002573094966	22.85060507329020
C	10.53171726048018	7.72753910146082	23.24676591566201
C	10.35124152302459	7.47304149603589	24.60106902396357
H	10.03264114394030	6.47906950938066	24.90090556242394
C	10.56314696750791	8.44313069089654	25.58037001451104
C	10.98074122956222	9.70710129367354	25.16117776080826
H	11.16041895179141	10.47997043156649	25.90307713352450
C	11.17813071107236	10.02012647177603	23.82273126840706
C	10.32067626841127	8.14821456232254	27.03838186777553
H	9.33036868918659	8.48882759406490	27.36173492672086
H	10.37569785586716	7.07643079681836	27.24062788976396
H	11.05421253346283	8.64739143727610	27.67629071238826
C	15.16003475216691	10.50351651812677	10.73561188548586
H	16.20148426698823	10.16216497684719	10.73375762724057
H	14.62397650034075	9.90180127859693	9.99770041804292
H	15.15935986184981	11.53878246756905	10.38713049650727
C	12.87949205400357	7.71190665201217	14.27075872257506
H	11.81528855155370	7.79401058966396	14.50522921165697
H	13.00397040963484	6.94691882127247	13.50249729681073
H	13.36745781033933	7.36762485343260	15.18603086863989
C	13.93384803056592	12.56408345759584	15.18063634548070
H	12.91266776862749	12.83369092278373	15.45971729884729
H	14.45747026847719	12.34764377094098	16.11562919504745
H	14.40375328767526	13.43114629938965	14.71442853434639
C	10.30226184599567	6.66297835369228	22.21125568792674
H	11.20056617046089	6.48886467378264	21.61288889099182
H	10.01182751671754	5.72178673628640	22.68024767969420
H	9.51936648338069	6.95213830782582	21.50590894453758
C	11.63503195557436	11.38640511334203	23.39591980479248
H	12.56824265170659	11.33425645170876	22.82868351797093
H	10.90521931247102	11.86544811377112	22.73796119104427
H	11.79225522533565	12.03038648127349	24.26241082551757

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