N-Aryl β-Diiminate Complexes of the Platinum Metals

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Supporting Information

Contents

Calculations

All calculations were carried out using Turbomole[1-6] coupled to an external geometry optimizer.[7, 8] Structures were fully optimized at the b3-lyp[9-11]/def-TZVP[12] level, and analytical frequencies were calculated to confirm the resulting stationary points were minima. Figure S1 shows the ligands studied, and Table S1 lists the calculated C-O stretch frequencies, their difference and average for these ligands bound to the $Rh(CO)_2$ fragment.. If ν_{avg} is taken as a measure of electron richness of the metal, a few conclusions can immediately be drawn:

- There is no major separation between 5-*e* and 3-*e* donors: the difference between Cp* and Cp (20 cm^{-1}) is larger than that between Cp and allyl (15 cm^{-1})!
- β-diiminates are good donors: depending on the substitution pattern they cover a range from Cp to allyl.
- Aminotroponimnates are very similar in donor properties to β-diiminates.
- Triazapentadienyls, diiminecyclopentadienyls, amidinates, dipyridylamides, formazanates, bis(pyrazolyl)borates, β-diketonates and carboxylates are all much poorer donors than β-diiminates.
- Introduction of CF_3 groups at the diiminate α carbons reduces the donating power strongly (20 cm^{-1}).

However, these values do not allow any definitive statement about the importance of π-donation by β-diiminate ligands.

References

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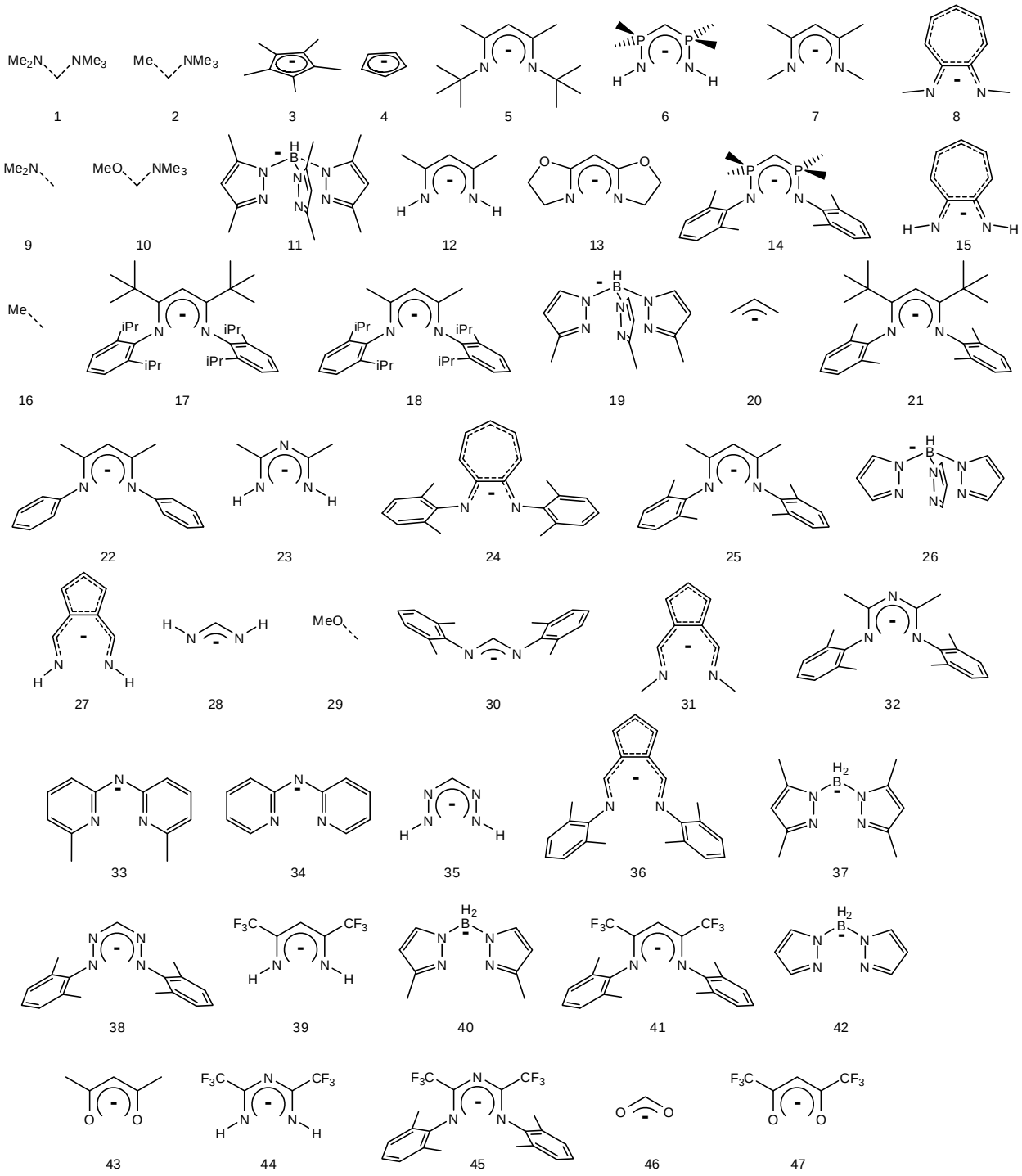

Figure S1. Ligands studied, in order of increasing calculated ν_{avg} of $LRh(CO)_2$.

Table S1. Calculated carbonyl stretch frequencies (cm^{-1}) for $LRh(CO)_2$ complexes.

	ν_1	ν_2	$\Delta\nu$	ν_{avg}
1	2006	2059	53	2032
2	2025	2095	69	2060
3	2039	2093	55	2066
4	2059	2115	56	2087
5	2055	2122	67	2089
6	2058	2121	63	2089
7	2062	2122	60	2092
8	2064	2120	56	2092
9	2061	2123	62	2092
10	2056	2131	75	2093
11	2065	2124	59	2094
12	2067	2124	56	2095
13	2067	2126	58	2097
14	2065	2129	65	2097
15	2071	2125	54	2098
16	2062	2135	73	2098
17	2070	2128	57	2099
18	2072	2129	57	2101
19	2072	2130	58	2101
20	2075	2128	53	2102
21	2073	2130	57	2102
22	2075	2132	57	2103
23	2075	2131	56	2103
24	2077	2130	53	2104
25	2076	2132	56	2104
26	2075	2133	58	2104
27	2079	2135	57	2107
28	2077	2138	61	2107
29	2077	2138	61	2108
30	2079	2138	58	2109
31	2079	2139	60	2109
32	2082	2138	56	2110
33	2080	2140	60	2110
34	2081	2139	58	2110
35	2089	2139	50	2114
36	2086	2144	58	2115
37	2087	2145	58	2116
38	2092	2141	49	2116
39	2092	2145	53	2119
40	2091	2148	58	2119
41	2094	2148	53	2121
42	2095	2151	56	2123
43	2094	2152	59	2123
44	2100	2153	52	2127
45	2101	2154	53	2127
46	2099	2160	61	2129
47	2119	2173	54	2146

X-ray structure of (C_6H_5C(NN-2,6-$Me_2C_6H_3)_2$)$Rh(CO)_2$ (arjan5: CCDC 937615)

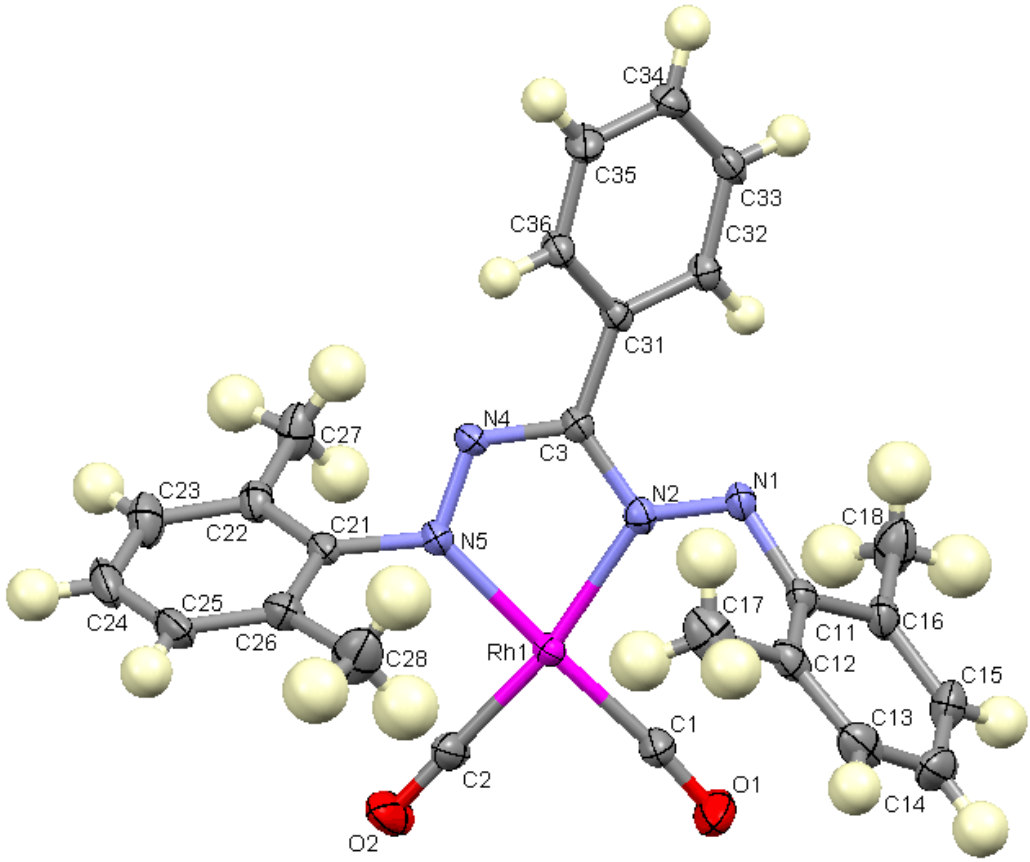

Figure S2. Thermal ellipsoid plot (35%) for (C_6H_5C(NN-2,6-$Me_2C_6H_3)_2$)$Rh(CO)_2$ (arjan5).

X-ray structure of (C_6H_5C(NN-2,6-$Me_2C_6H_3)_2$)Rh(1,5-COD) (arjan6: CCDC 937616)

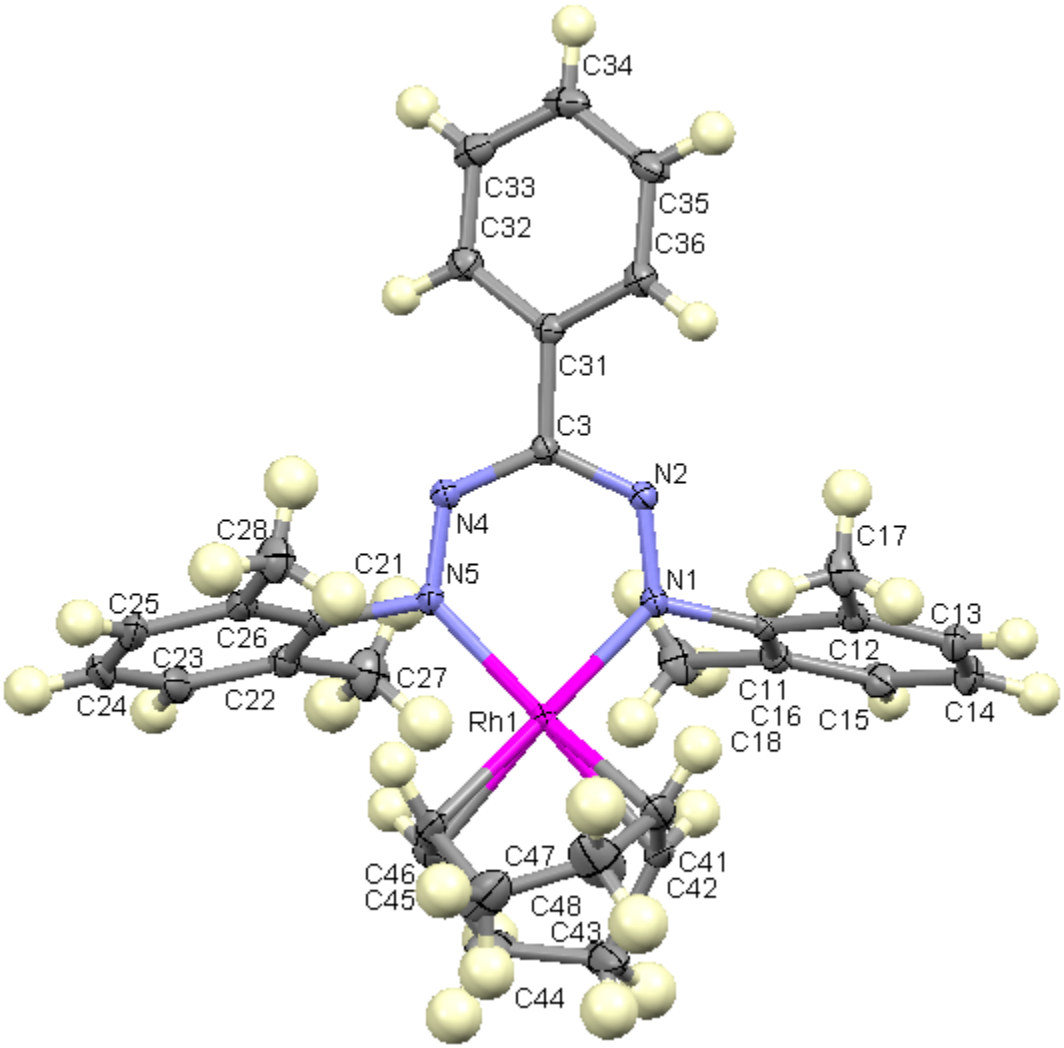

Figure S3. Thermal ellipsoid plot (35%) for (C_6H_5C(NN-2,6-$Me_2C_6H_3)_2$)Rh(1,5-COD) (arjan6).

X-ray structure of ($C_6H_5C(NNC_6H_5)(NN\text{-}2,6\text{-}Me_2C_6H_3))Rh(CO)_2$ (arjan7: CCDC 937617)

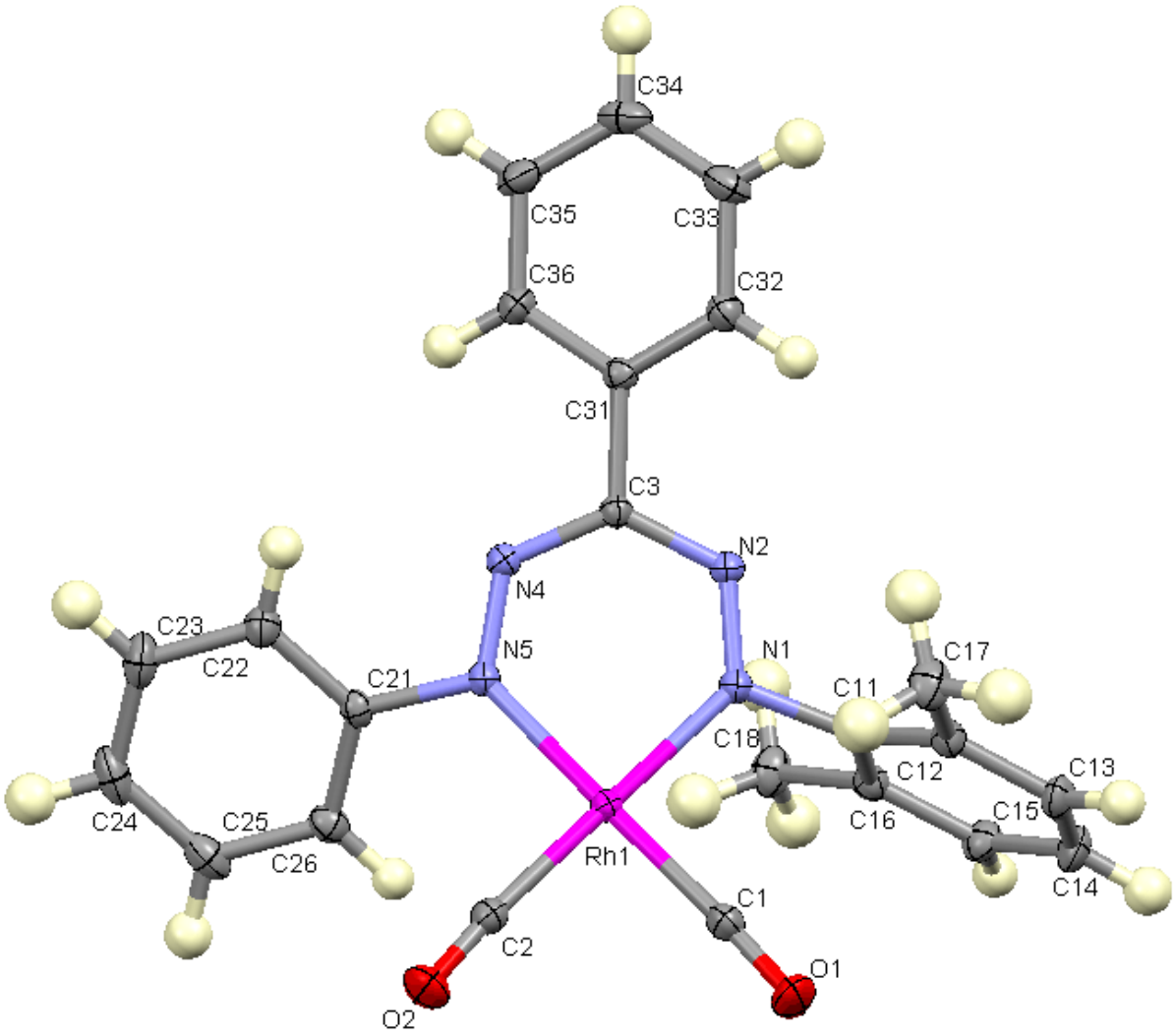

Figure S4. Thermal ellipsoid plot (35%) for ($C_6H_5C(NNC_6H_5)(NN\text{-}2,6\text{-}Me_2C_6H_3))Rh(CO)_2$ (arjan7).