TOC of the Supporting Information:

Section S1 – Further electrochemical data

The electrochemical properties of all title compounds (**1** – **7**) were probed with the aid of cyclic voltammetry in order to determine if the coordinated metal fragment has an influence on the redox-potential of the iron atom. Electrochemical studies have been performed on silicon-, tin- and germanium-bridged ferrocenophanes by the groups of Manners and Pannell.[S3-1] We have consequently used the electrolyte $[NBu_4][Al\{OC(CF_3)_3\}_4]$[S3-2] for our studies.

[S3-1] (a) V. V. Dement'ev, F. Cervantes-Lee, L. Parkanyi, H. Sharma, K. H. Pannell, *Organometallics* **1993**, *12*, 1983. (b) K. H. Pannell, V.V. Dement'ev, H. Li, F. Cervantes-Lee, M. T. Nguyen, A. F. Diaz, *Organometallics* **1994**, *13*, 3644. (c) J. K. Pudelski, D. A. Foucher, C. H. Honeyman, A. J. Lough, I. Manners, *Organometallics* **1995**, *14*, 2470. (d) on tin-bridged Ferrocenophanes: H. K. Sharma, F. Cervantes-Lee, J. S. Mahmoud, K. H. Pannell, *Organometallics* **1999**, *18*, 399. (e) on Germanium-bridged Ferrocenophanes: M. Castruita, F. Cervantes-Lee, J. S. Mahmoud, Y. Zhang, K. H. Pannell, *J. Organomet. Chem.* **2001**, *637-639*, 664.

[S3-2] I. Raabe K. Wagner, K. Guttsche, M. Wang, M. Grätzel, G. Santiso-Quiñonoes, I. Krossing, *Chem. Eur. J.* **2009**, *15*, 1966.

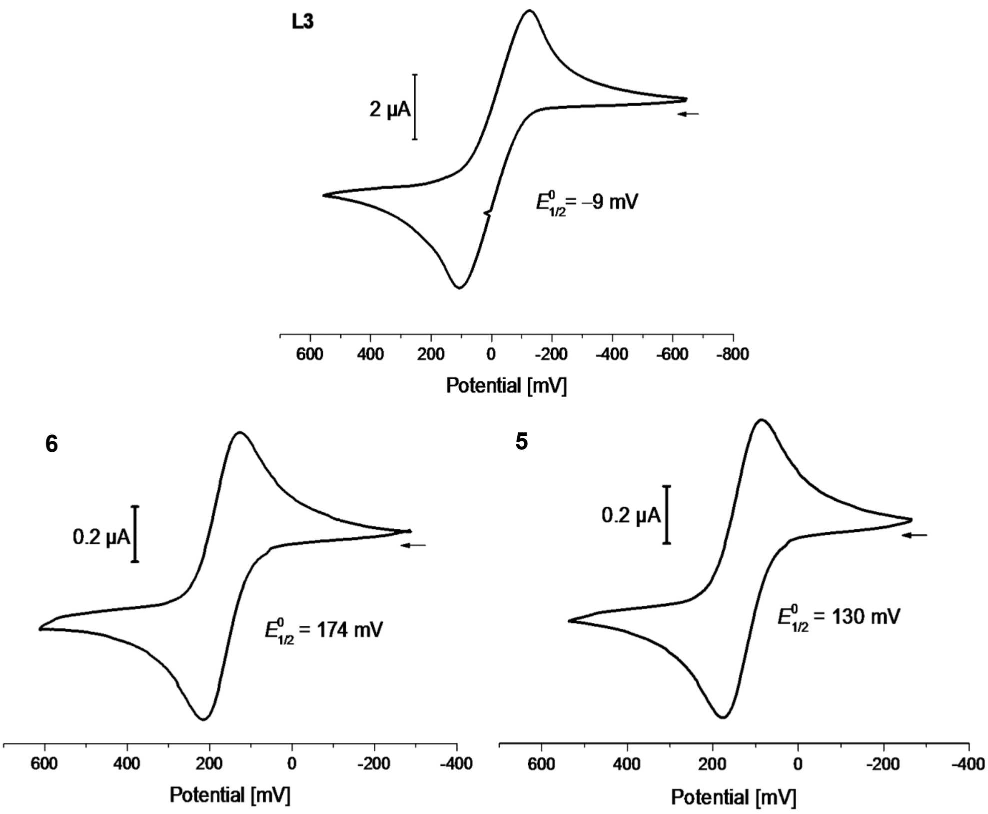

Figure S1-1. Cyclic voltammograms **L3** and its Pd complexes **6** and **5** in CH_2Cl_2 *vs* Fc/Fc^+; v = 100 mV/s, Pt/$[NBu_4][Al\{OC(CF_3)_3\}_4]$/Ag.

Section S2 – Further details on the redox-switchable catalysis

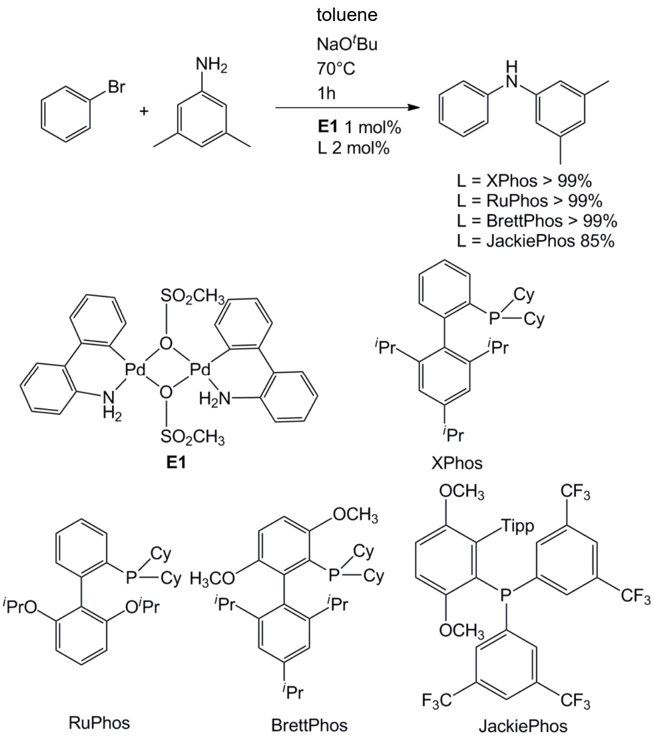

Figure S2-1. Reaction of bromobenzene and 3,5-dimethylaniline using classic Buchwald ligands. Cy = cyclohexyl, Tipp = 2,4,6-triisopropylphenyl.

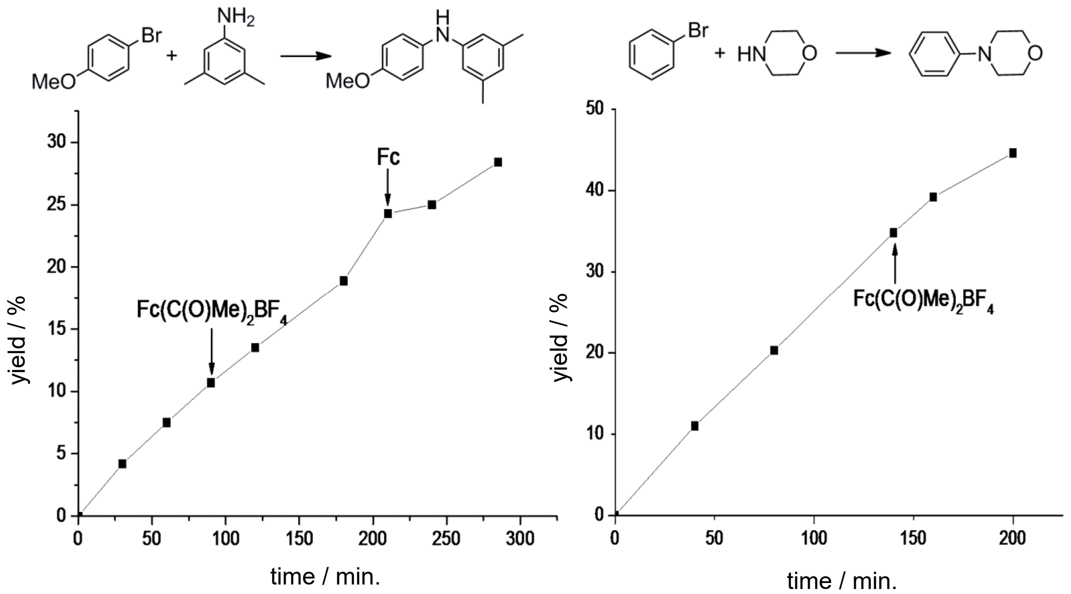

Figure S2-2. Reaction progress of the conversions of 1-bromo-4-methoxybenzene with 3,5-dimethylaniline (left) and that of bromobenzene with morpholine (right) determined by ^{1}H NMR spectroscopy. Conditions: toluene-D8, NaO*t*Bu, 2 mol% **4**, 85°C. Fc = ferrocene(yl).

Section S3 – Selected NMR spectra

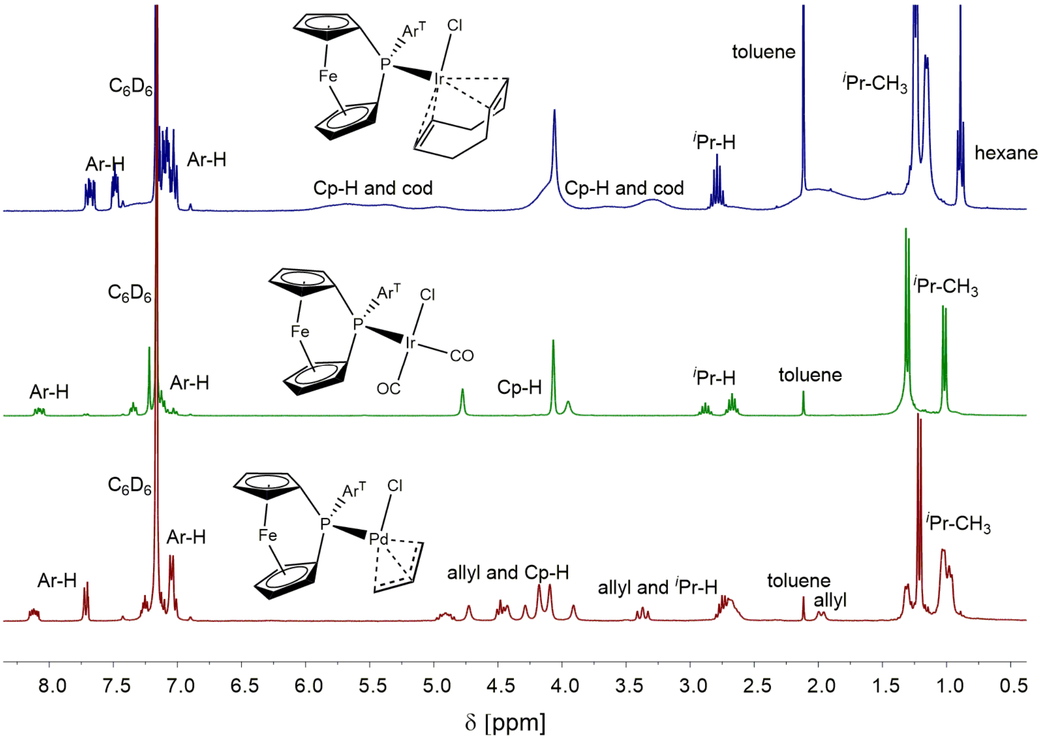

Figure S3-1. ^{1}H NMR spectra of **1** (top), **2** (middle), and **4** (bottom) in C_6D_6.

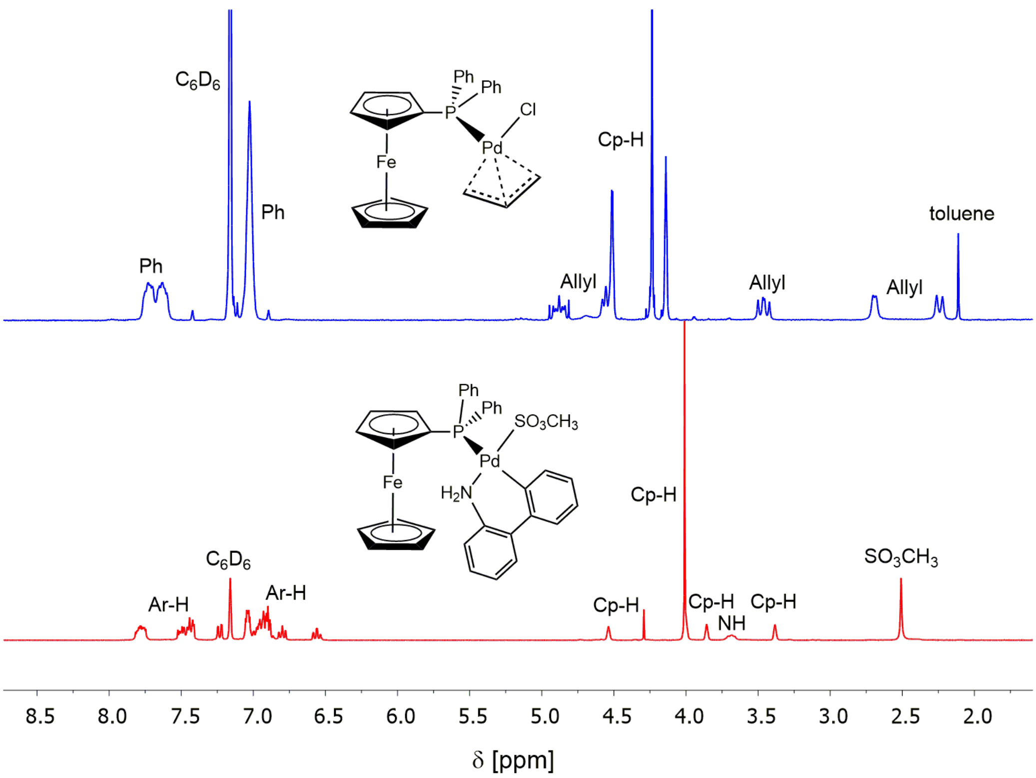

Figure S3-2. ^{1}H NMR spectra of **5** and **6** in C_6D_6.

Section S4 – Compilation of the IR data

IR-spectra were measured using the ATR technique (attenuated total reflection) on a Bruker Vertex 70 spectrometer in the range from 4000 cm^{-1} to 400 cm^{-1}. The intensity of the absorption band is indicated as vw (very weak), w (weak), m (medium), s (strong), vs (very strong), and br (broad) and are quoted in cm^{-1}.

$FcPAr^T$ (**L2**): ṽ = 414 (w), 441 (m), 475 (vs), 496 (m), 537 (s), 599 (w), 624 (vw), 652 (w), 663 (w), 704 (m), 731 (w), 746 (vs), 763 (vs), 780 (w), 802 (s), 843 (vw), 851 (vw), 877 (vs), 920 (vw), 939 (w), 1000 (w), 1017 (m), 1028 (w), 1053 (w), 1068 (vw), 1098 (vw), 1115 (w), 1167 (vw), 1186 (vw), 1239 (vw), 1315 (vw), 1360 (m), 1380 (m), 1430 (w), 1458 (s), 1541 (vw), 1567 (vw), 1583 (vw), 1606 (w), 2027 (vw), 2167 (vw), 2866 (m), 2926 (m), 2957 (vs), 3050 (vw).

[Ir(κ^1*P*-**L2**)(cod)Cl] (**1**): ṽ = 417 (w), 432 (vs), 454 (vs), 465 (s), 483 (vs), 503 (s), 529 (w), 541 (s), 549 (s), 589 (w), 603 (m), 630 (vw), 650 (w), 668 (vw), 677 (w), 694 (m), 729 (vs), 765 (m), 777 (w), 809 (m), 857 (vw), 869 (w), 882 (vw), 901 (vw), 939 (vw), 972 (w), 1003 (m), 1012 (m), 1033 (w), 1080 (vw), 1102 (w), 1115 (vw), 1124 (vw), 1158 (vw), 1188 (w), 1213 (vw), 1246 (vw), 1294 (w), 1316 (vw), 1359 (w), 1379 (w), 1431 (w), 1457 (m), 1495 (vw), 1557 (vw), 1605 (vw), 2033 (vw), 2050 (vw), 2149 (vw), 2169 (vw), 2189 (vw), 2839 (w), 2866 (w), 2917 (w), 2951 (w), 2983 (vw), 3021 (vw), 3122 (vw).

[Ir(κ^1*P*-**L2**)$(CO)_2$Cl] (**2**): ṽ = 422 (vs), 442 (m), 468 (m), 480 (vs), 506 (m), 532 (vs), 557 (m), 601 (m), 632 (vw), 650 (vw), 669 (vw), 679 (vw), 700 (vw), 711 (vw), 740 (s), 768 (m), 810 (w), 840 (vw), 854 (vw), 874 (w), 899 (vw), 918 (vw), 939 (vw), 960 (vw), 1017 (w), 1031 (vw), 1054 (vw), 1078 (vw), 1100 (vw), 1122 (w), 1164 (vw), 1190 (w), 1247 (vw), 1261 (vw), 1294 (vw), 1317 (vw), 1332 (vw), 1360 (vw), 1382 (w), 1426 (vw), 1440 (vw), 1461 (vw), 1493 (vw), 1540 (vw), 1558 (vw), 1585 (vw), 1604 (vw), 1994 (vs, C≡O), 2067 (vs, C≡O), 2117 (vw), 2161 (vw), 2864 (vw), 2928 (vw), 2956 (w), 3056 (vw).

[AuCl(κ[1]*P*-**L2**)] (**3**): ṽ = 398 (w), 433 (m), 468 (m), 483 (s), 500 (m), 537 (m), 556 (m), 605 (w), 651 (w), 682 (w), 713 (w), 750 (m), 763 (s), 810 (w), 817 (m), 830 (vw), 857 (vw), 873 (w), 884 (vw), 900 (vw), 924 (vw), 939 (vw), 980 (vs), 1021 (w), 1063 (m), 1099 (vs), 1118 (vs), 1190 (s), 1231 (vs), 1296 (vw), 1308 (vw), 1361 (vw), 1383 (w), 1430 (vw), 1461 (w), 1506 (vw), 1520 (vw), 1541 (vw), 1559 (vw), 1602 (vw), 1635 (vw), 1651 (vw), 1684 (vw), 1701 (vw), 2867 (vw), 2929 (vw), 2954 (w), 3077 (vw), 3101 (vw).

[Pd(κ[1]*P*-**L2**)(allyl)Cl] (**4**): ṽ = 400 (m), 435 (m), 463 (m), 477 (vs), 489 (s), 499 (s), 525 (w), 541 (vs), 602 (w), 620 (vw), 631 (vw), 650 (vw), 678 (w), 695 (vw), 710 (vw), 730 (vw), 749 (w), 771 (vs), 811 (m), 829 (vw), 854 (w), 874 (m), 893 (w), 935 (w), 956 (w), 1017 (s) 1034 (w), 1053 (vw), 1067 (vw), 1078 (vw), 1102 (vw), 1120 (w), 1162 (w), 1185 (w), 1214 (vw), 1255 (w), 1293 (vw), 1314 (vw), 1359 (w), 1381 (w), 1424 (w), 1456 (w), 1507 (vw), 1558 (vw), 1603 (vw), 1981 (vw), 2006 (vw), 2042 (vw), 2163 (vw), 2173 (vw), 2205 (vw), 2862 (w), 2927 (w), 2962 (m), 3050 (vw), 3079 (vw), 3093 (vw).

[Pd(κ[1]*P*-**L3**)(allyl)Cl] (**5**): ṽ = 406 (w), 435 (m), 452 (s), 460 (vs), 484 (vs), 492 (vs), 517 (m), 545 (m), 566 (vw), 598 (vw), 630 (vw), 692 (vs), 744 (s), 825 (m), 848 (vw), 887 (vw), 916 (vw), 923 (vw), 942 (vw), 1006 (w), 1029 (w), 1057 (vw), 1094 (w), 1166 (w), 1187 (vw), 1305 (vw), 1382 (vw), 1409 (vw), 1435 (w), 1482 (w), 1572 (vw), 1586 (vw), 1607 (vw), 1950 (vw), 1971 (vw), 2164 (vw), 2848 (vw), 2916 (vw), 3016 (vw), 3049 (vw).

[Pd(κ[1]*P*-**L3**)(2-aminobiphenyl)(SO_3CH_3)] (**6**): ṽ = 402 (w), 441 (w), 456 (m), 471 (vs), 484 (s), 500 (vs), 522 (s), 542 (s), 618 (w), 628 (w), 695 (s), 739 (s), 772 (w), 805 (vw), 828 (w), 863 (vw), 935 (vw), 1000 (m), 1021 (s), 1030 (s), 1043 (s), 1062 (w), 1098 (m), 1151 (vs), 1198 (vw), 1234 (m), 1312 (vw), 1333 (vw), 1389 (vw), 1418 (w), 1434 (w), 1461 (vw), 1480 (vw), 1494 (vw), 1572 (vw), 1616 (vw), 1913 (vw), 1984 (vw), 2025 (vw), 2109 (vw), 2161 (vw), 2183 (vw), 2218 (vw), 3047 (w), 3109 (w), 3200 (w), 3272 (vw).

[Pd(κ^1*P*-**L1**)(2-aminobiphenyl)(SO_3CH_3)] (**7**): ṽ = 389 (vw), 403 (w), 419 (vw), 450 (s), 476 (vw), 498 (m), 527 (m), 541 (m), 559 (s), 597 (vw), 616 (vw), 632 (w), 682 (vw), 696 (vw), 736 (m), 750 (s), 772 (w), 809 (vw), 852 (vw), 881 (vw), 934 (vw), 1001 (m), 1019 (vs), 1058 (vw), 1142 (m), 1183 (vw), 1245 (m), 1291 (vw), 1380 (vw), 1419 (vw), 1439 (vw), 1461 (vw), 1492 (vw), 1572 (vw), 1605 (vw), 1652 (vw), 1683 (vw), 1715 (vw), 1948 (vw), 1962 (vw), 1974 (vw), 1992 (vw), 2009 (vw), 2024 (vw), 2054 (vw), 2088 (vw), 2150 (vw), 2163 (vw), 2182 (vw), 2197 (vw), 2214 (vw), 2924 (vw), 2958 (vw), 3110 (vw).