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Preparation of Unsymmetrical Diaryl Selenides via S_NAr Reactions in η^6 -Chloroarene Transition Metal Complexes

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4-(*tert*-Butoxycarbonyl)phenyl phenyl selenide (4c). 1H NMR δ 1.57 (s, 9H),

7.30-7.40 (m, 5H), 7.55 (m, 2H), 7.83 (d, J = 8.7 Hz, 2H). ^{13}C NMR δ 28.1 q, 81.0 s,

128.3 d, 129.1 s, 129.6 d, 130.0 d, 130.2 s, 130.6 d, 134.6 d, 138.6 s, 165.4 s.

4-(*tert*-Butoxy carbonyl)phenyl 4-(dimethylamino)phenyl selenide (4d). 1H

NMR δ 1.55 (s, 9H), 2.99 (s, 6H), 6.68 (d, J = 8.9 Hz, 2H), 7.2 (d, J = 8.4 Hz, 2H),

7.48 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H). ^{13}C NMR δ 28.2 q, 40.2 q, 80.8 s,

112.2 s, 113.2 d, 128.2 d, 129.2 s, 129.7 d, 137.7 d, 141.9 s, 150.8 s, 165.6 s.

4-(1,3-Dioxolan-2-yl)phenyl phenyl selenide (4e). 1H NMR δ 3.97-4.20 (m, 4H),

5.78 (s, 1H), 7.27 (m, 3H), 7.38 (dm, J = 7.4 Hz, 2H), 7.46 (m, 4H). ^{13}C NMR δ 65.3 t,

103.3 d, 127.3 d, 127.4 d, 129.3 d, 130.8 s, 132.5 s, 132.7 d, 133.1 d, 137.0 s.

4-(1,3-Dioxolan-2-yl)phenyl 4-dimethylaminophenyl selenide (4f). 1H NMR δ

2.98 (s, 6H), 3.92-4.18 (m, 4H), 5.74 (s, 1H), 6.66 (d, J = 9.0 Hz, 2H), 7.28 (br s, 4H),

7.47 (d, J = 9.0 Hz, 2H). ^{13}C NMR δ 40.3 q, 65.2 t, 103.5 d, 113.1 d, 113.4 s, 127.0 d,

129.6 d, 135.5 s, 136.0 s, 137.1 d, 150.5 s.

4-Acetylphenyl phenyl selenide (4g). ^1H NMR δ 2.56 (s, 3H), 7.34-7.40 (m, 5H), 7.59 (m, 2H), 7.79 (d, J = 8.4 Hz, 2H). ^{13}C NMR δ 26.5 q, 128.4 s, 128.6 d, 128.9 d, 129.7 d, 130.2 d, 135.0 s, 135.1 d, 140.3 s, 197.3 s.

4-Acetylphenyl 4-chlorophenyl selenide (4h). ^1H NMR δ 2.57 (s, 3H), 7.32 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.7 Hz, 2H). ^{13}C NMR δ 26.5 q, 126.8 s, 129.0 d, 129.9 d, 130.5 d, 134.9 s, 135.4 s, 136.2 d, 139.5 s, 197.3 s.

4-Acetylphenyl 4-(dimethylamino)phenyl selenide (4i). ^1H NMR δ 2.53 (s, 3H), 3.01 (s, 6H), 6.67 (d, J = 9.0 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 9.0 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H). ^{13}C NMR δ 26.4 q, 40.2 q, 111.5 s, 113.2 d, 128.1 d, 128.7 d, 134.3 s, 137.8 d, 143.5 s, 150.9 s, 197.4 s.

1,3-Bis[4-(dimethylamino)phenylseleno]benzene (4j). ^1H NMR δ 2.98 (s, 12H), 6.64 (d, J = 9.0 Hz, 4H), 6.97 (m, 3H), 7.25 (m, 1H), 7.43 (d, J = 9.0 Hz, 4H). ^{13}C NMR δ 40.3 q, 113.1 d, 113.3 s, 127.0 d, 129.4 d, 130.2 d, 135.5 s, 137.1 d, 150.5 s.

η^6 -[3-[4-(Dimethylamino)phenylseleno]chlorobenzene]tricarbonylchromium (3b). ^1H NMR δ 3.03 (s, 6H), 4.89 (d, J = 6.2 Hz, 1H), 5.18 (d, J = 6.5 Hz, 1H), 5.31 (br s, 1H), 5.39 (t, J = 6.4 Hz, 1H), 6.70 (d, J = 9.0 Hz, 2H), 7.55 (d, J = 9.0 Hz, 2H).

η^6 -[1,3-Bis[4-(dimethylamino)phenylseleno]benzene] tricarbonylchromium (3c). ^1H NMR δ 3.01 (s, 12H), 4.91 (br d, J = 6.4 Hz, 2H), 5.23 (t, J = 6.4 Hz, 1H), 5.27 (br s, 1H), 6.67 (d, J = 8.6 Hz, 4H), 7.50 (d, J = 8.6 Hz, 4H).

3-(Phenylseleno)phenyl 4-(dimethylamino)phenyl selenide (5). ^1H NMR δ 2.98 (s, 6H), 6.63 (d, J = 9.1 Hz, 2H), 7.05 (t, J = 7.6 Hz, 1H), 7.11 (d t, J = 7.8, 1.6 Hz, 1H), 7.18 (d t, J = 7.3, 1.7 Hz, 1H), 7.24 (m, 3H), 7.34 (t, J = 1.6 Hz, 1H), 7.43 (m, 4H).

^{13}C NMR δ 40.2 q, 112.8 s, 113.1 d, 127.4 d, 128.1 d, 129.3 d, 129.61 d, 129.64 d, 130.4 s, 132.2 s, 132.8 d, 133.3 d, 136.1 s, 137.3 d, 150.5 s.

η^6 -(4-Chlorophenylseleno)benzene- η^5 -(cyclopentadienyl)iron

hexafluorophosphate (9b). ^1H NMR (acetone- d_6) δ 5.22 (s, 5H), 6.43 (m, 1H), 6.46-6.52 (m, 4H), 7.58 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 8.6 Hz, 2H). ^{13}C NMR (acetone- d_6) δ 79.3 d, 87.5 d, 89.1 d, 89.2 d, 102.3 s, 125.1 s, 131.5 d, 137.1 s, 139.1 d.

η^6 -(4-Methoxyphenylseleno)benzene- η^5 -(cyclopentadienyl)iron

hexafluorophosphate (9c). ^1H NMR (acetone- d_6) δ 3.90 (s, 3H), 5.17 (s, 5H), 6.33-6.39 (m, 3H), 6.44 (t, J = 6.3 Hz, 2H), 7.13 (d, J = 8.9 Hz, 2H), 7.81 (d, J = 8.9 Hz, 2H). ^{13}C NMR (acetone- d_6) δ 56.0 q, 79.1 d, 87.0 d, 87.8 d, 88.8 d, 104.7 s, 115.7 s, 117.1 d, 140.0 d, 162.7 s.

η^6 -[4-(Dimethylamino)phenylseleno]benzene- η^5 -(cyclopentadienyl)iron

hexafluorophosphate (9d). ^1H NMR (acetone- d_6) δ 3.07 (s, 6H), 5.15 (s, 5H), 6.30 (d, J = 6.2 Hz, 2H), 6.34 (t, J = 5.9 Hz, 1H), 6.42 (t, J = 6.2 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 7.66 (d, J = 8.9 Hz, 2H). ^{13}C NMR (acetone- d_6) δ 40.2 q, 79.0 d, 86.7 d, 87.2 d, 88.6 d, 106.1 s, 114.4 d, 139.6 d, 152.9 s.

η^6 -(Phenylseleno)-2-methylbenzene- η^5 -(cyclopentadienyl)iron

hexafluorophosphate (9e). ^1H NMR (acetone- d_6) δ 2.68 (s, 3H), 5.14 (s, 5H), 6.06 (d, J = 6.0 Hz, 1H), 6.27-6.36 (m, 2H), 6.55 (d, J = 5.9 Hz, 1H), 7.54-7.64 (m, 3H), 7.83 (d, J = 8.2 Hz, 2H). ^{13}C NMR (acetone- d_6) δ 21.3 q, 79.3 d, 87.1 d, 87.5 d, 88.4 d, 89.9 d, 102.7 s, 103.9 s, 126.3 s, 131.2 d, 131.6 d, 137.5 d.

η^6 -(4-methoxyphenylseleno)-2-methylbenzene- η^5 -(cyclopentadienyl)iron

hexafluorophosphate (9f). ^1H NMR (acetone- d_6) δ 2.67 (s, 3H), 3.91 (s, 3H), 5.11 (s,

5H), 5.90 (dd, $J = 5.8, 1.6$ Hz, 1H), 6.24-6.31 (m, 2H), 6.52 (dd, $J = 5.8, 1.6$ Hz, 1H), 7.15 (dm, $J = 8.9$ Hz, 2H), 7.80 (dm, $J = 8.9$ Hz, 2H). ^{13}C NMR (acetone- d_6) δ 21.0 q, 56.0 q, 79.2 d, 86.7 d, 86.8 d, 87.2 d, 89.8 d, 101.8 s, 105.9 s, 115.3 s, 117.3 d, 140.1 d, 162.8 s.

η^6 -[4-(Dimethylamino)phenylseleno]-2-methylbenzene- η^5 -(cyclopentadienyl)-iron hexafluorophosphate (9g). ^1H NMR (acetone- d_6) δ 2.65 (s, 3H), 3.08 (s, 6H), 5.07 (s, 5H), 5.85 (m, 1H), 6.22-6.27 (m, 2H), 6.48 (m, 1H), 6.90 (dm, $J = 9.0$ Hz, 2H), 7.64 (dm, $J = 9.0$ Hz, 2H). ^{13}C NMR (acetone- d_6) δ 20.9 q, 40.2 q, 79.13 d, 86.0 d, 86.3 d, 86.9 d, 89.6 d, 101.5 s, 107.2 s, 108.3 s, 114.6 d, 139.7 d, 153.0 s.

η^6 -1,2-Bis(4-chlorophenylseleno)benzene- η^5 -(cyclopentadienyl)iron hexafluorophosphate (9h). ^1H NMR (acetone- d_6) δ 5.22 (s, 5H), 6.36-6.42 (m, 4H), 7.57 (dm, $J = 8.5$ Hz, 4H), 7.85 (dm, $J = 8.5$ Hz, 4H). ^{13}C NMR (acetone- d_6) δ 80.7 d, 88.2 d, 90.6 d, 103.0 s, 126.7 s, 131.5 d, 137.0 s, 138.3 d.

η^6 -1,3-Bis(4-chlorophenylseleno)benzene- η^5 -(cyclopentadienyl)iron hexafluorophosphate (9i). ^1H NMR (acetone- d_6) δ 5.19 (s, 5H), 6.25 (br s, 1H), 6.42-6.46 (m, 2H), 6.50 (m, 1H), 7.53 (dm, $J = 8.5$ Hz, 4H), 7.77 (dm, $J = 8.5$ Hz, 4H). ^{13}C NMR (acetone- d_6) δ 80.9 d, 86.9 d, 88.0 d, 88.6 d, 102.8 s, 124.7 s, 131.5 d, 137.3 s, 139.2 d.

η^6 -1,4-Bis(4-chlorophenylseleno)benzene- η^5 -(cyclopentadienyl)iron hexafluorophosphate (9j). ^1H NMR (acetone- d_6) δ 5.20 (s, 5H), 6.45 (s, 4H), 7.55 (dm, $J = 8.5$ Hz, 4H), 7.83 (dm, $J = 8.5$ Hz, 4H). ^{13}C NMR (acetone- d_6) δ 81.0 d, 88.66 d, 101.0 s, 125.0 s, 131.5 d, 137.2 s, 139.2 d.